UNIT 5
ORGANIC CHEMISTRY

INTRODUCTION

Carbon can form more compounds than probably any other elements because of its ability to form single, double and triple bonds also build chain (polymer) and ring structures. The compounds formed by carbon are thought to be the most essential and central to all life on this planet. The study of carbon compounds is called Organic Chemistry.

Organic chemistry is classified into different classes depending on the **functional group** present in the molecule. *A functional group is a group of atoms, which gives the chemical behavior of the molecule.* Some of the functional groups are listed in the table 5.1. We will discuss some of these functional groups throughout this topic.

All organic compounds are derived from a group of compounds called hydrocarbons. Hydrocarbons are compounds that contain only carbon and hydrogen atoms. Hydrocarbons are classified as shown in the diagram below.

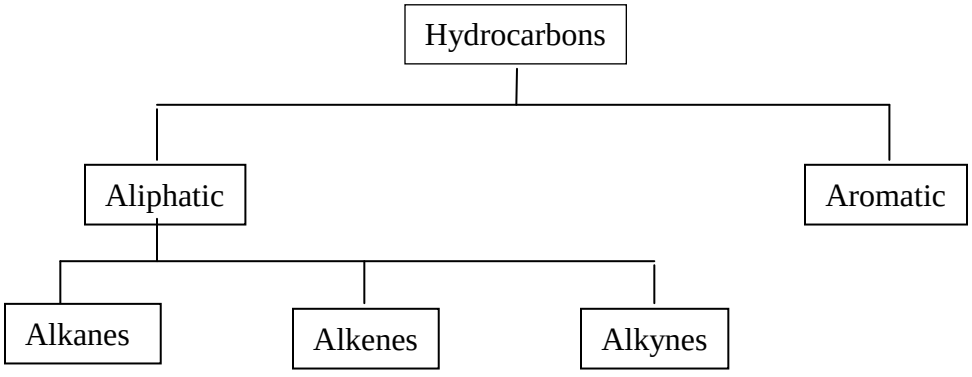
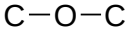
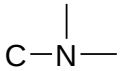
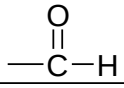
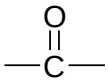
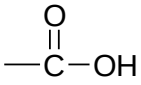
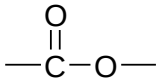
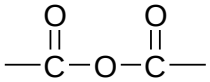
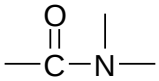
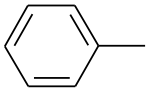


Figure 5.1: Classification of hydrocarbons

Table 5.1: Classes of Organic compounds depending on the Functional groups

Class	Functional group
alkene	
alkyne	
alcohol	
ether	
amine	
aldehyde	
ketone	
carboxylic acid	
ester	
acid anhydride	
amide	
benzene	

ALKANES

Alkanes have a general formula of C_nH_{2n+2}, where n=1,2,3… The feature of alkanes is that the molecules will only contain C-C single covalent bond, therefore are known as **saturated hydrocarbons**. The first four hydrocarbons are called methane, ethane, propane, and butane. The name of the members of this series end with "**ane**". The names for several of the alkanes are listed in Table 5.2.

Table 5.2: The Normal Alkanes (or n-alkanes)

Name	**# of carbons**	**Structure**	**Melting Point (^{0}C)**	**Boiling Point (^{0}C)**
Methane	1	CH_4	-182.5	-161.6
Ethane	2	CH_3CH_3	-182.3	-88.6
Propane	3	$CH_3CH_2CH_3$	-187.9	-42.1
Butane	4	$CH_3(CH_2)_2CH_3$	-138.3	-0.5
Pentane	5	$CH_3(CH_2)_3CH_3$	-129.8	36.1
Hexane	6	$CH_3(CH_2)_4CH_3$	-95.3	68.7
Heptane	7	$CH_3(CH_2)_5CH_3$	-90.6	98.4
Octane	8	$CH_3(CH_2)_6CH_3$	-56.8	125.7
Nonane	9	$CH_3(CH_2)_7CH_3$	-53.5	150.8
Decane	10	$CH_3(CH_2)_8CH_3$	-29.7	174.0
Undecane	11	$CH_3(CH_2)_9CH_3$	-25.6	195.9
Dodecane	12	$CH_3(CH_2)_{10}CH_3$	-9.6	216.3

In the alkane series, an increase in the number of carbon atoms in the hydrocarbon increases the melting and the boiling point. Also the increase in carbon atom in the hydrocarbon changes its physical property, that is C1-C4 is a gas, C5-C8 is liquid and C8> is a solid.

Did you know…?

- *Methane is produced when vegetables decompose anaerobically in the presence of bacteria.*
- *Termites are the natural source of methane.*

CHEMICAL STRUCTURES OF ALKANES

Chemists have devised ways to represent organic compounds to draw informative structures. Some of the representations are shown in figure 5.2.

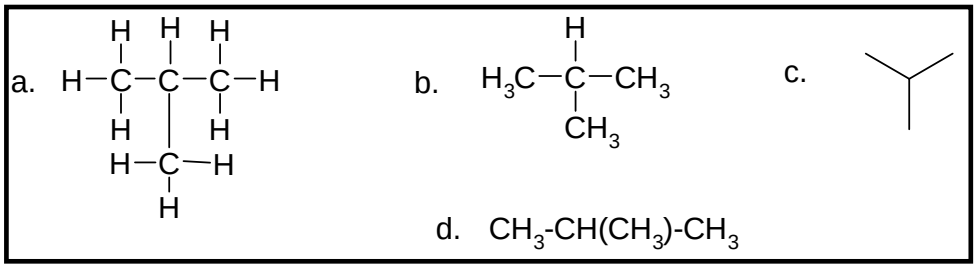


Figure 5.2: Different arrangement of 2-methylpropane.
a. Structural formula – shows all atoms attached.
b. Abbreviated structure.
c. Skeletal structure- shows the carbon skeleton. H atoms are avoided however, other atoms like N,O, Cl are shown.
d. Abbreviated structure where branching is shown in brackets.

STRUCTURAL ISOMERISM IN ALKANES

The structural formula for the first 4 alkanes: methane, ethane, propane and butane are given below in Figure 5.3. 2-methylpropane is a **structural isomer** of butane.

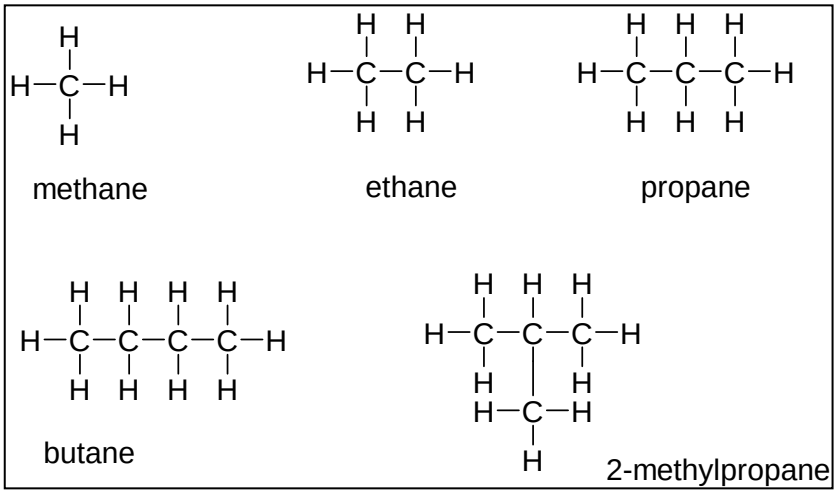
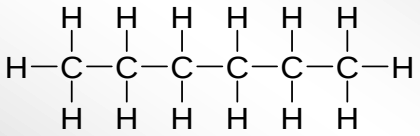


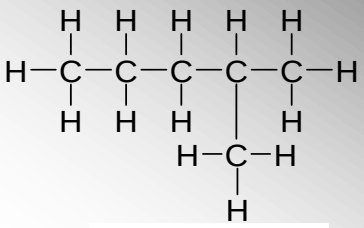
Figure 5.3: Structural formulas of some alkanes

Methane, ethane and propane have only one possible structure, however, butane has two possible structures. The two structures of C_4H_{10}, *n*-butane and 2-methylpropane (isopropane) are called structural isomers (see figure 5.3). ***Structural isomers*** *therefore are molecules that have same molecular formula but different structural formula.* (This is discussed in more detail later in this chapter). The structure of n-butane is called a straight chain and its isomer- 2-methylpropane will be a branched alkane. As the number of carbon atoms in the molecule increases the number of structural isomers also increases.

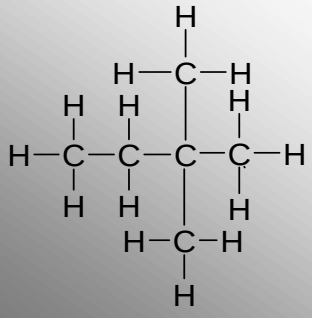
Example: How many structural isomers can be identified in hexane



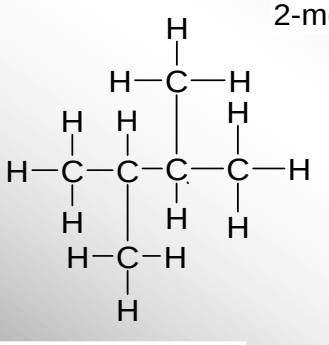
n-hexane



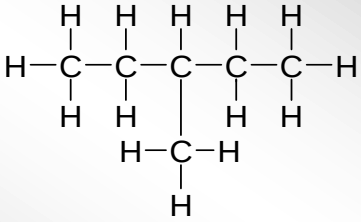
2-methylpentane



2,2-dimethylbutane



2,3-dimethylbutane



3-methylpentane

BRANCHED ALKANES

Alkyl Groups

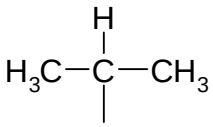
Alkyl groups are substituent whose names are obtained by replacing the **–ane** with **–yl**

—CH_3	— CH_2CH_3	—$CH_2CH_2CH_3$
methyl	ethyl	propyl

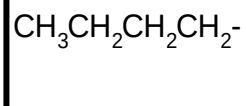
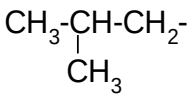
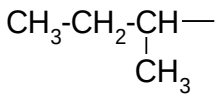
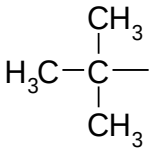
For alkanes with more than two carbons, have more than one derived group. Two groups can be derived from propane:

1. Removal of terminal hydrogen gives: $CH_3CH_2CH_2$— propyl

2. Removal of inner hydrogen gives: isopropyl group

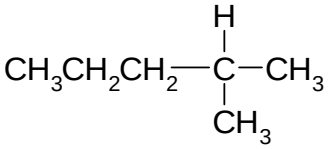


There are four alkyl groups that contain four carbon atoms each:

			
butyl	isobutyl	sec-butyl	tert-butyl

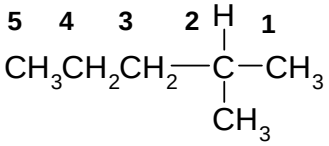
Nomenclature of Branched Alkanes:

a. Locate the longest continuous chain of carbon atoms, which determines the parent name of the alkane.



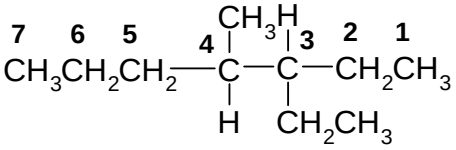
Longest chain is 5 C pentane

b. Number the carbon chain beginning with the end of the chain nearest to the branching.



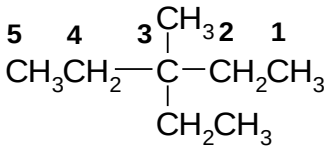
2-methypentane

c. Designate the location of each subtituent group using a number, and list the groups alphabetically. (Apply rules as above)



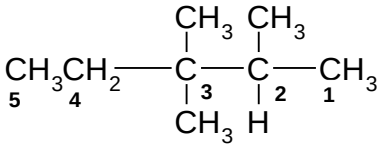
3-ethyl-4-methylheptane

d. When two or more substituent is present on the same carbon use that number twice.



3-ethyl-3-methylpentane

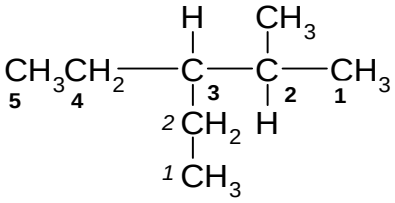
e. When two or more substituents are identical the are indicated by the use of prefixes; di , tri, or tetra.



2,3,3-trimethylpentane

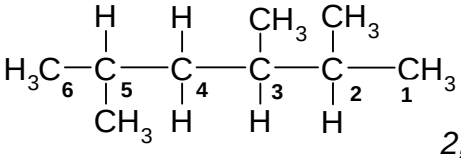
> ***NOTE:***
>
> ***When writing names, consider the following:***
> - ***Numbers are separated by commas.***
> - ***Numbers and the names are separated by dash.***
> - ***There is no space between the parent name and the substituent names.***

f. When two chains of equal length compete for the selection as the base chain, choose the chain with the greater number of substituent.



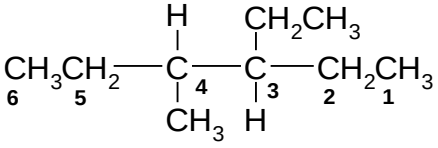
3-ethyl-2-methylpentane (numbering in bold)
and not
3-isopropylpentane (numbering in italics)

g. When branching first occurs at an equal distance from either end of the longest chain, choose the numbering that gives the lower positions to the substituents.



2,3,5-trimethylhexane (numbering in bold)
and not
2,4,5-trimethylhexane (numbering in opposite direction)

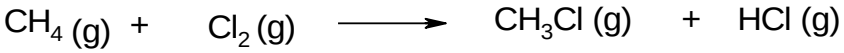
h. When two or more side chains are in equivalent position, the one to assigned the lower number is that cited first in the name of alphabetical order.



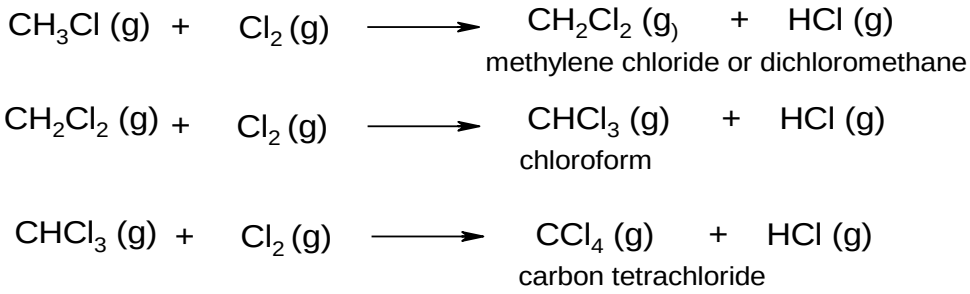
3-ethyl-4-methylhexane
and not
4-ethyl-3-methylhexane

REACTIONS OF ALKANES

Alkanes are considered to be fairly unreactive due to its strong single covalent bonds in the molecule. However under special conditions alkanes will undergo substitution reaction in which the hydrogen atoms are replaced by halogen atoms. For example, when methane and chlorine is heated above 100°C or irradiated with light, methyl chloride is produced.



If excess chlorine gas is present, then the reaction will proceed further.



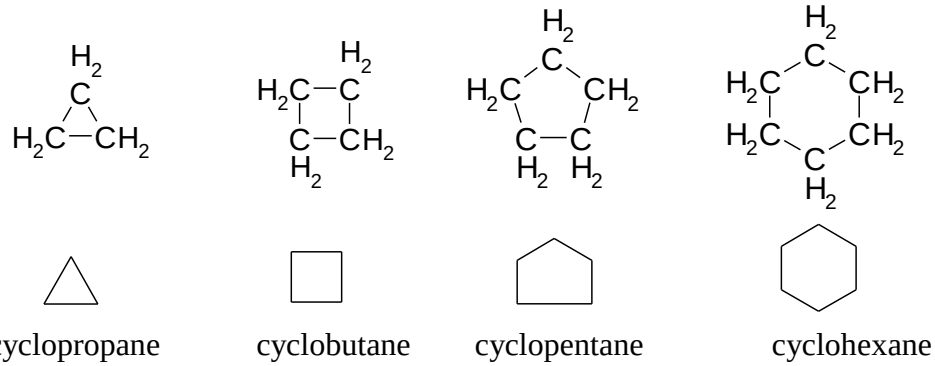
methylene chloride or dichloromethane

chloroform

carbon tetrachloride

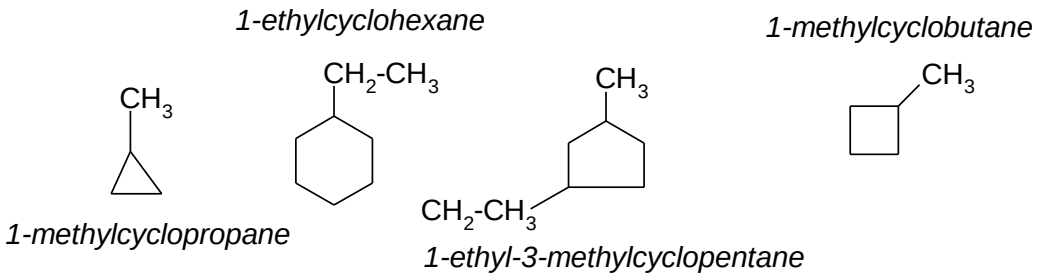
CYCLOALKANES

Cycloalkanes have one ring and are named by attaching "**cyclo"** to the name of alkanes possessing the same number of carbon atoms.



cyclopropane cyclobutane cyclopentane cyclohexane

Substituted cycloalkanes are named as alkyl cycloalkanes (rings are normally drawn without showing the carbons and the hydrogens as shown below)

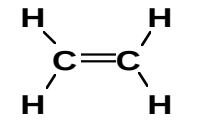


ALKENES

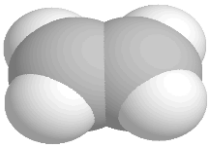
The alkenes contain at least one carbon to carbon double bond. Alkenes have the general formula C_nH_{2n}, where n= 2,3... The members of the alkene series are listed in the table 5.3 below.

Table 5.3: The first 7 members of the alkenes

Name	# carbon atoms	Molecular Formula
Ethene or ethylene	2	C_2H_4
Propene	3	C_3H_6
Butene	4	C_4H_8
Pentene	5	C_5H_{10}
Hexene	6	C_6H_{12}
Heptene	7	C_7H_{14}
Octene	8	C_8H_{16}

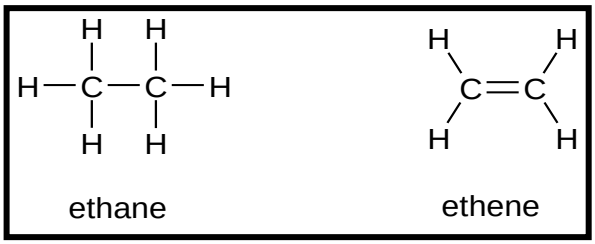


Ethylene (an alkene)



ISOMERISM IN ALKENES

In alkanes such as ethane, C_2H_6, the rotation of the molecule about the carbon to carbon single bond (sigma bond, δ) is quite free. However, it is different for alkenes such as ethene. Ethene, C_2H_4, in addition to a sigma bond, the molecule also has a pi bond (π) between the two carbon atoms and it is this pi bond that restrict the rotation of the carbon to carbon double bond.



Because of the restricted rotation about C=C bond, groups on the adjacent carbons are either *cis* or *trans* to each other as shown in figure 5.4. The term *cis* means the two groups are adjacent to each other (same side of the double bond) and *trans* means the two groups are across to each other (opposite side of the double bond). The two isomers are called **geometric isomers** *as they have the same chemical bonds but different spatial arrangements*.

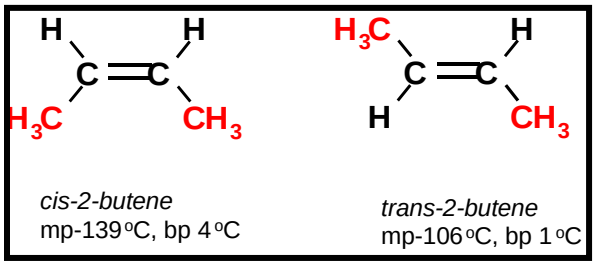
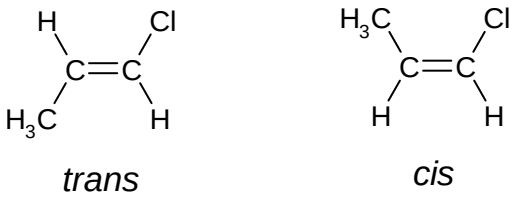


Figure 5.4: Geometric isomer of 2-butene

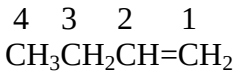
Example: Draw the geometric isomers of chloropropene



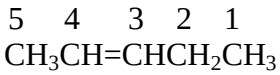
Did You Know…?
The retina in the eyes contains the molecule rhodopsin, which responds to light. Rhodopsin consists of 11-cis retinal and the protein opsin. When the retina receives the light, double bond breaks which allows 11-*cis* retinal to isomerise to all-*trans* retinal and the electrical signal is generated and transmitted to the brain which forms the image.

NOMENCLATURE OF ALKENE

(a) Unbranched hydrocarbons having one double bond are named by replacing the "**ane**" of the corresponding alkane by "**ene**". Designate the position of the double bond giving it the lowest possible number.

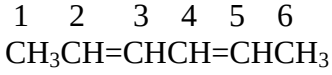


But-1-ene
(or 1-Butene)



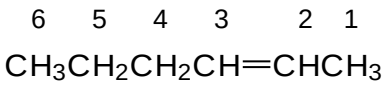
Pent-2-ene
(or 2-Pentene)

(b). If there are two or more double bonds the ending will "**adiene**", "**atriene**" etc.

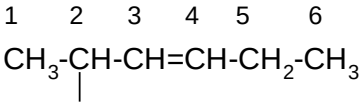


2,4-hexadiene

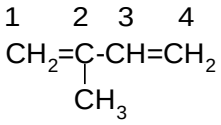
(c). Follow IUPAC rules given for alkanes for numbering and naming substituents



2-hexene



2-methyl-3-hexene



2-methyl-1,3-butadiene

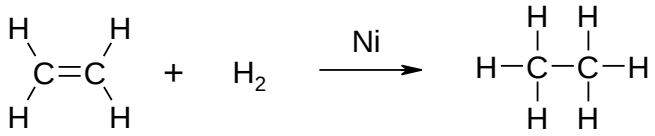
REACTIONS OF ALKENE

Alkenes are **unsaturated hydrocarbons** because it contains at least one carbon to carbon double bond. They are more reactive than saturated hydrocarbons. Unsaturated hydrocarbons commonly undergo addition reactions in which one molecule adds to the hydrocarbon forming a single product. Examples of addition reaction in alkenes are hydrogenation, halogenation, hydrohalogenation and hydration.

Hydrogenation

Hydrogenation is the addition of hydrogen and is an important process in the food industry. This reaction is achieved when unsaturated hydrocarbons are heated with catalyst (such as nickel, platinum or palladium) at high temperature and pressure in presence of hydrogen gas.

The reaction below is a hydrogenation reaction in which hydrogen is added to ethene to produce ethane. The two hydrogen atoms get added to the two carbon atoms that had a double bond.



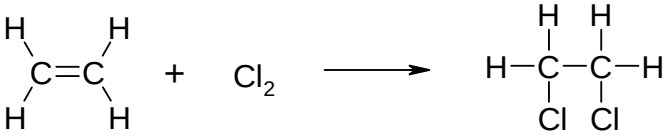
ethene ethane

Did You Know…?

Margarine is prepared by hydrogenation of vegetable oils. Vegetable oils are heated with catalyst nickel in presence of hydrogen under controlled conditions to achieve the desired texture of margarine.

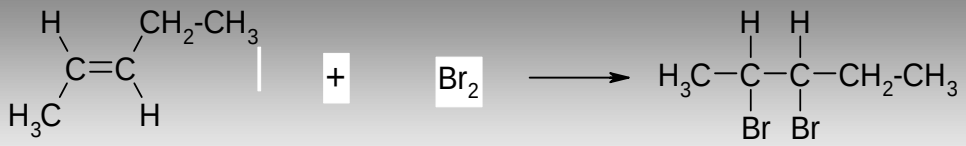
Halogenation

Halogenation is the addition of halogen (bromine, chlorine, fluorine and iodine) to the double bond.



Addition of chlorine to ethene yields dichloroethane.

Example: What will be the product when bromine is reacted with 2-pentene?

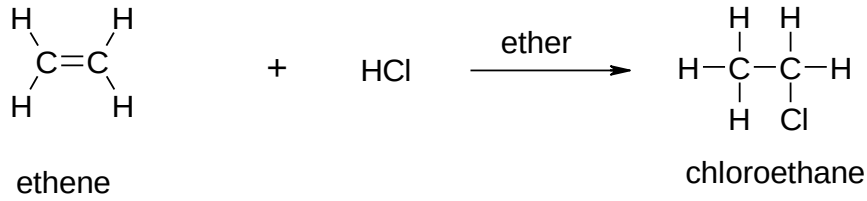


2-pentene 2,3-dibromopentane

In the above reaction of 2-pentene with bromine, the disappearance of the red brown color can be observed.

Hydrohalogenation

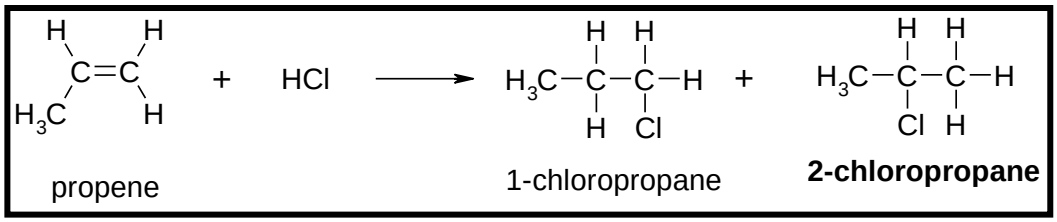
In this type of reaction, molecules such as HCl, HBr, HF and HI are added to alkenes. These reactions are facilitated by the presence of ether. Addition of HCl to ethene producing chloroethane is given below.



ethene chloroethane

Ethene is a symmetrical alkene, so only one product is formed. However, in unsymmetrical alkenes two products are possible as shown in figure 5.5. But in reality for the example shown below, only one product, 2-chloropropane is formed.

Figure 5.5: Possible product is formed in addition of unsymmetrical alkene.

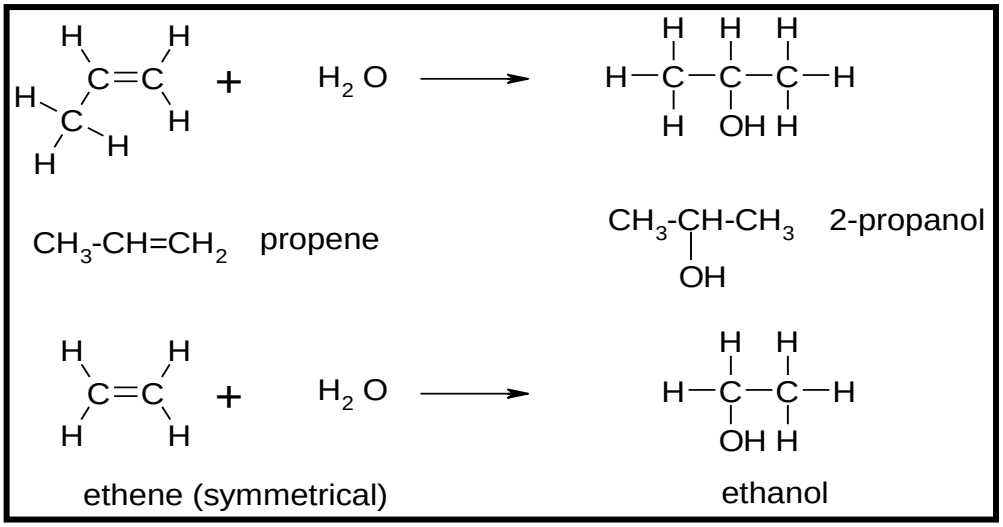


propene 1-chloropropane **2-chloropropane**

In 1871, a Russian chemist Vladimir Markovnikov postulated a generalisation called ***Markovnikovs rule,*** which help in the determination of the product formed. ***Markovnikovs rule states that in addition of molecules in unsymmetrical alkenes, the hydrogen gets added to the carbon with more hydrogens.***

Hydration

Hydration is the addition of water to the alkene. Hydration of an unsymmetrical alkene such as propene will yield 2-propanol as it follows the ***Markovnikovs rule***. For this reaction to occur, the water molecule splits into H^+ and OH^- ions. The H^+ ions bind to the double bond carbon with two hydrogens and the OH^- ions binds to the double bond carbon with one hydrogen only. However, for a symmetrical alkene like ethene, ***Markovnikovs rule*** does not apply.



Reaction with acidified potassium permanganate

Oxidising reagents such potassium permanganate ($KMnO_4$) in neutral or acidic solutions cleaves alkenes giving carbonyl-containing (C=O) products such as aldehydes, ketones and carboxylic acids. Although the actual reaction that takes place is a lot more complicated, it can be simply said that the molecule breaks into two at the double bond as shown in figure 5.6 and an oxygen atom binds at the double bond carbons. If one of the carbons with C=O has two hydrogen atoms, then it will be further oxidized to formic acid. At room temperature, formic acid easily decomposes to carbondioxode and hydrogen gas.

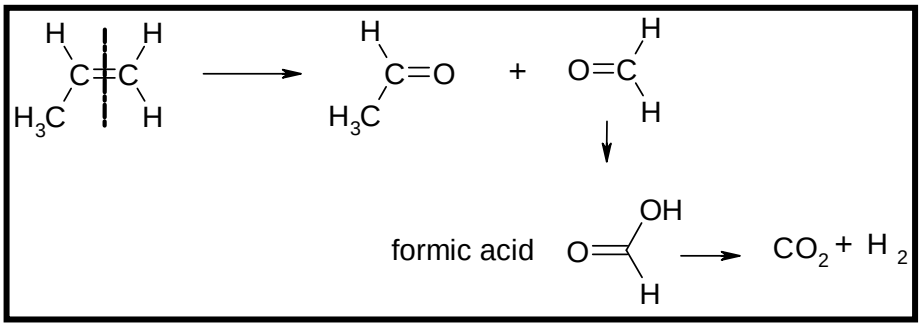
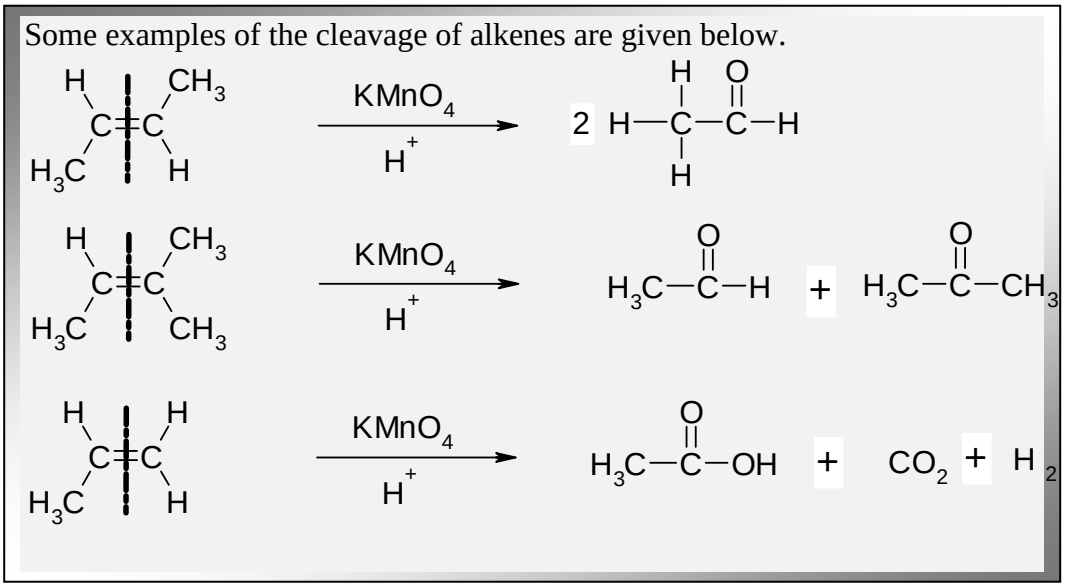
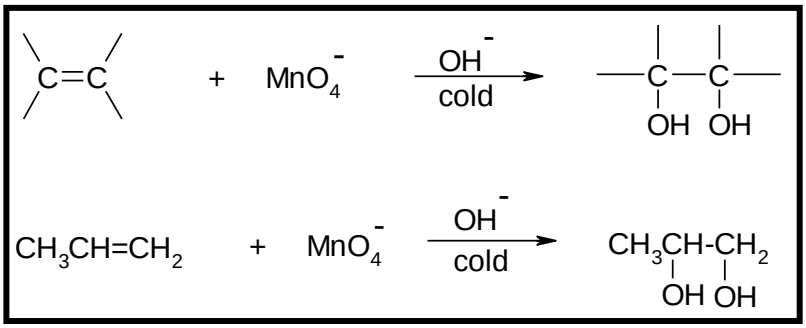


Figure 5.6: Oxidative cleavage of alkenes with acidified $KMnO_4$.

Some examples of the cleavage of alkenes are given below.



However, if alkenes react with cold potassium permanganate ($KMnO_4$) and hydroxide ion (OH-), then oxidation of π bond occurs without the cleavage of the sigma bond (σ) producing a **diol**.



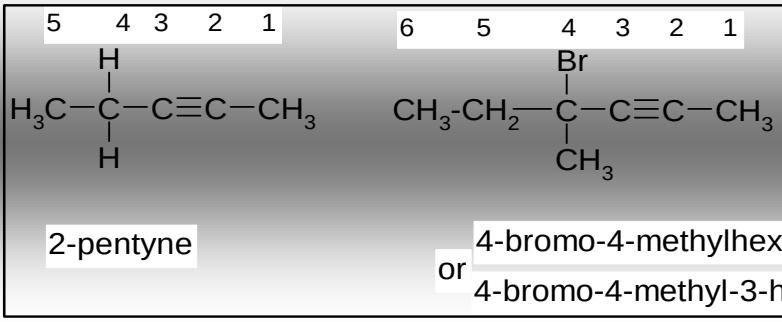
ALKYNES

Alkynes contain at least one carbon to carbon triple bond. They have the general formula of C_nH_{2n-2}, where n= 2,3,4... (number of carbon atoms)

Alkyne Nomenclature:

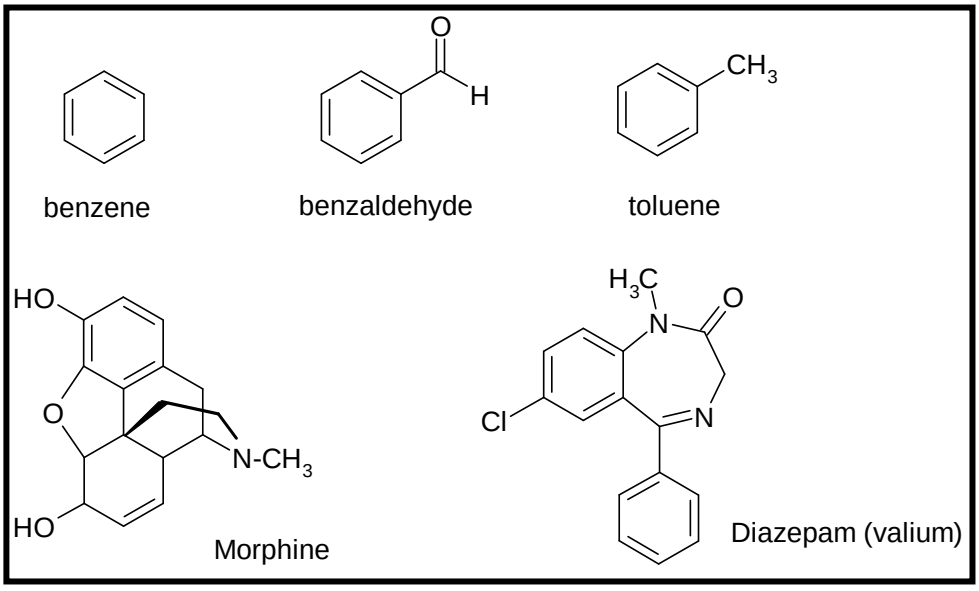
(a). Alkynes have the suffix –yne and the position of the triple bond is indicated by the lowest possible number in the longest chain.
(b). Indicate the substituents on the longest chain (as in alkanes) in alphabetical order.

Examples:



AROMATIC HYDROCARBONS

The word aromatic refers to the hydrocarbon benzene and its structural relatives. Some of aromatic compounds are benzene, benzaldehyde, toluene (methyl benzene), morphine (a well known analgesic) and diazepam (synthetic tranquilizer) are given below:



Did You Know…?

- Benzene causes bone marrow depression and leukopenia (reduction in white blood cells).

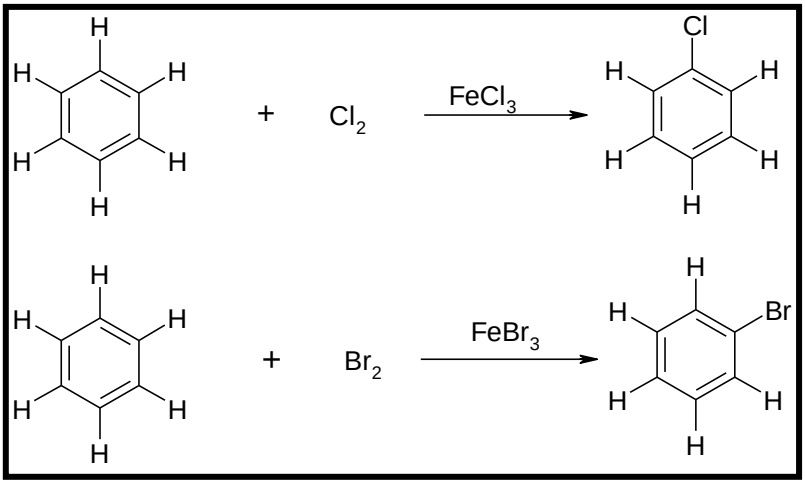
BENZENE SHOULD BE HANDLED WITH CARE AND SHOULD NOT BE INHALED.

Reaction of Benzene

Benzene is very unreactive because it is very stable. The stability of the molecule is as a result of ***delocalisation*** (electrons are not confined to the two carbons that form the double bond but spread within the ring) of double bond electrons.

However, benzene can be reacted with halogens under special conditions. This reaction is **substitution reaction,** helps benzene maintain its double bond electrons and this reaction is possible when a catalyst, Iron halide is used.

Examples of substitution reaction in benzene with halogen are given below.



ISOMERISM IN CARBON COMPOUNDS

Isomers are different compounds that have the same molecular formula. Many isomers exist in organic chemistry, which can be classified into two groups: **structural isomers** and **stereoisomers.** This classification is shown by Figure 5.7 below

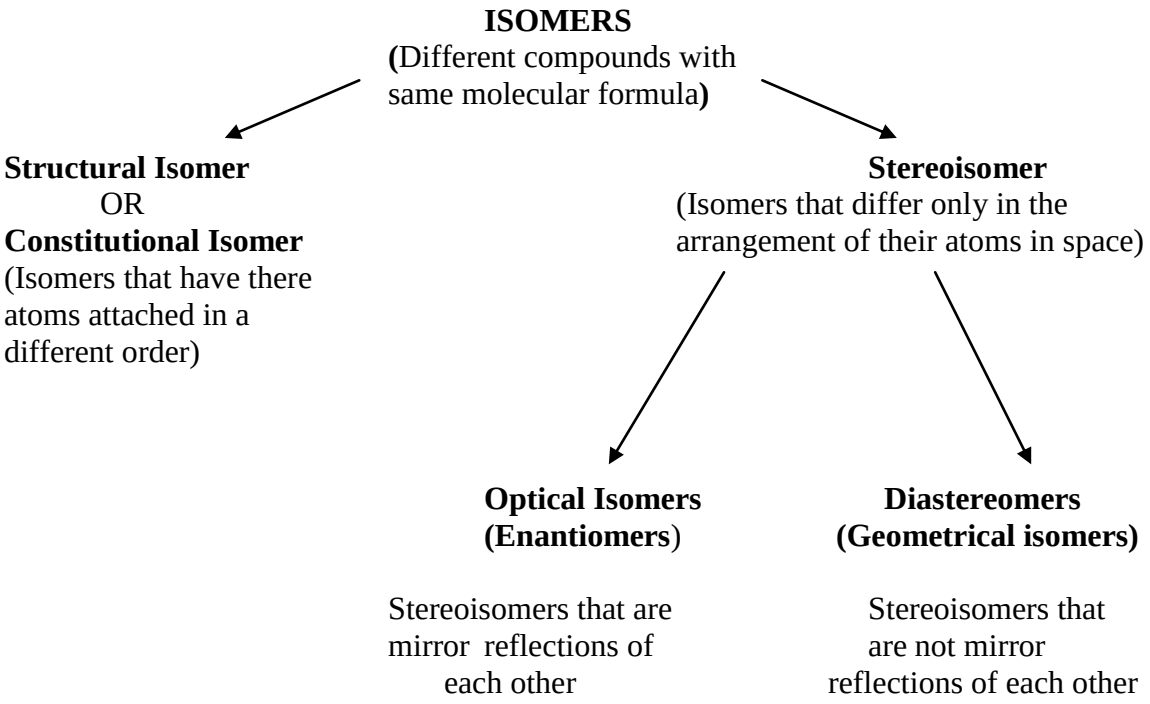
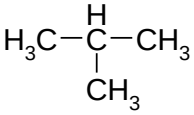
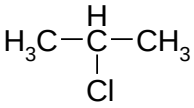
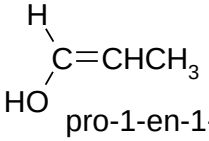
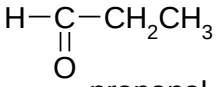


Figure 5.7: Classification of Isomerism in carbon compounds.

Structural Isomers

Structural isomers differ because their atoms are attached in a different order (see table 5.4).

Table 5.4: Some structural Isomers

Molecular formula	Type of structural isomer	Examples	
C_4H_{10}	chain isomer	$CH_3CH_2CH_2CH_3$ butane	 2-methylpropane
C_3H_7Cl	positional isomer	$CH_3CH_2CH_2Cl$ 1-chloropropane	 2-chloropropane
C_2H_6O	functional group isomer	CH_3CH_2OH ethanol	CH_3-O-CH_3 dimethylether
C_3H_6O	tautomerism	 pro-1-en-1-ol	 propanal

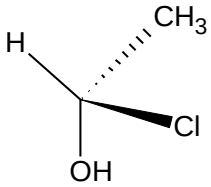
Stereoisomers

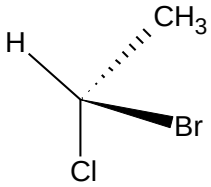
Stereoisomers have their constituent atoms attached in the same order. They only differ in arrangement of their atoms in space. Stereoisomers can be subdivided into two categories: enantiomers and diastereomers.

Enantiomers: are stereoisomers whose molecule are mirror reflections of each other. It only occurs with those compounds whose molecules are chiral.

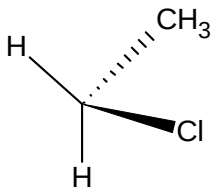
Chiral atoms: A chiral carbon atom is an atom that has four different (asymmetric atoms) groups attached to it.

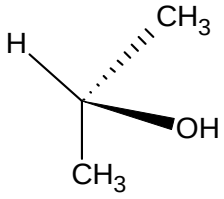
A chiral molecule is defined as one that is not superimposible on its mirror image. For example:





Examples of Achiral molecules are:



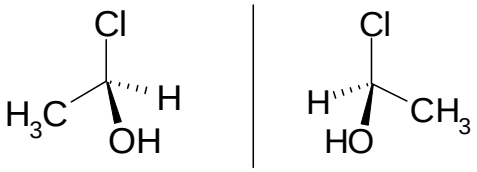


2 same groups, i.e 2 H-atoms
therefore not chiral (achiral)

2 CH_3 groups
therefore achiral molecule

Chirality of a molecule containing one chiral carbon is shown below:

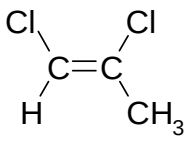
Example:

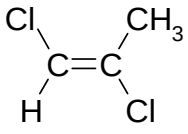


Both molecules are mirror image of each other but cannot be put on top of each other exactly, and therefore are not superimposable.

Diastereomers

These are stereoisomers whose molecules are not mirror reflection of each other. Note the positions of the CH_3 groups on the carbon atoms that have the double bond. The pi bond forces the molecule to be planar and does not allow free rotation of groups, therefore the geometry is fixed.





* not mirror immages
* no free rotation
* are planar

cis-1,2-dichloropropene

trans-1,2-dichloropropene

cis means: on the same side
trans means: on the opposite sides.

ALCOHOLS

When a hydrogen atom on a hydrocarbon is replaced by the *hydroxyl functional group*, – OH is called **alcohols**. This OH group does not react with bases although it may have some acidic character. After an OH group has replaced the hydrogen atom, the general formula of alcohols then becomes $C_nH_{2n+1}OH$ 'OR' $C_nH_{2n+2}O$.

The alcohols are named by replacing the terminal **"e"** of the corresponding alkane by "**ol**". Common names treat the alkyl group as substituent followed by the word alcohol as in the table 5.5 below. Some of the common alcohols are also shown in figure 5.8.

Table 5.5: Some Common alcohols

	CH_3OH	CH_3CH_2OH	$(CH_3)_3COH$	$(CH_3)_3CCH_2OH$
Common Name	Methyl alcohol	Ethyl alcohol	t-butyl alcohol	Neo pentyl alcohol
IUPAC Names	Methanol	Ethanol	2-methylpropan-2-ol	2,2-dimethylpropan-1-ol

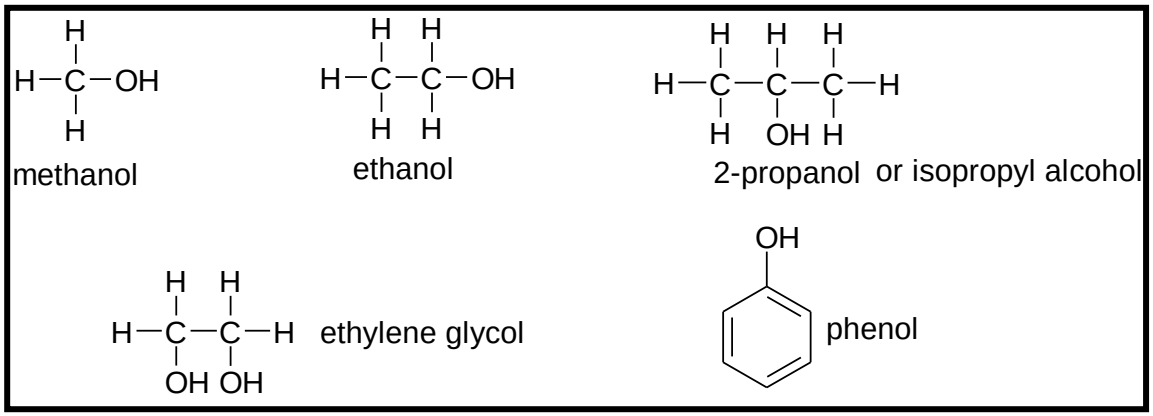


Figure 5.8: Some common alcohols

Ethanol is the very well known among alcohols. It is prepared biologically by the fermentation of sugars (or starch/ carbohydrates) such as grains, grapes and potatoes in presence of bacterial cultures or yeast.

$$C_6H_{12}O_6\,(aq) \xrightarrow{\text{enzymes}} 2\ CH_3CH_2\text{-}OH\,(aq) + CO_2(g)$$

Ethanol has many uses as solvent in organic reactions, and as starting materials for the manufacture of dyes, drugs, cosmetics and explosives. It is also a component of the alcoholic bevarages as it is regarded as the least toxic alcohol. Human bodies produce an enzyme alcohol dehydrogenase that helps in the metabolism of ethanol to acetaldehyde and hydrogen gas.

$$CH_3CH_2OH \xrightarrow[dehydrogenase]{alcohol} CH_3CHO + H_2(g)$$

Did You Know…?

Ethanol depresses the central nervous system, increases the production of stomach acids and dilates blood vessels. This explains why excessive drinkers have big bellies.

Methanol is also called **wood alcohol** because it was once prepared by dry distillation of wood. It is highly toxic as it can cause nausea and blindness if a few milliliters in consumed.

2-propanol is used to clean skin before minor surgery and to sterilize medical instruments.

CLASSIFICATION OF ALCOHOLS

Type of alcohol	1^0 (Primary)	2^0 (Secondary)	3^0 (Tertiary)
# of R (alkyl) Groups attached to the carbon with the –OH	1	2	3
Structure	$R\text{-}CH_2\text{-}OH$	$R\text{-}\underset{\displaystyle R}{\underset{\vert}{CH}}\text{-}OH$	$\overset{\displaystyle R}{\overset{\vert}{R\text{-}CH}}\text{-}OH$ $\vert$ R

PROPERTIES OF ALCOHOL

Volatility: Ethanol (Mr= 46) is far less volatile compared to compounds with a similar relative molecular mass such as propane (Mr=44) and chloromethane (Mr=50.5)

Boiling points: Boiling points of alcohols are far higher than its corresponding alkanes (see table 5.6)

Table 5.6: Boiling points of Some alcohols and alkanes

Alkanes	**Boiling point (°C)**	**Alcohol**	**Boiling point (°C)**
Methane	-161.6	Methanol	64.7
Ethane	-88.6	ethanol	78.3
Propane	-42.1	Propanol	97.2
Butane	-0.5	Butanol	117.7
Pentane	36.1	Pentanol	138.0`
Hexane	68.7	Hexanol	157.5

Solubility: ethanol are generally more soluble in water.

Hydrogen bonding in ethanol: The cause of the properties in ethanol such as increased volatility, high boiling points and solubility is due to **hydrogen bonding.** Hydrogen bonds form between –OH groups of adjacent ethanol molecules as shown in figure 5.9. This bonding gives high intermolecular forces, holds the molecules together and therefore the volatility is low. Also the hydrogen bonding between ethanol and water shows that ethanol is soluble and miscible. Hydrogen bonds are strong intermolecular forces and therefore require a lot of energy to break these bonds, thus boiling point is very high.

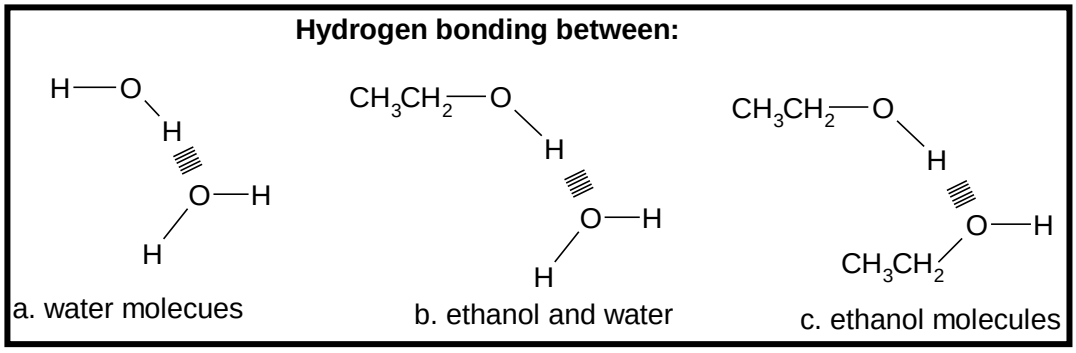


Figure 5.9: Hydrogen bonding in ethanol

REACTIONS OF ALCOHOLS

1. With phosphorous pentachloride (PCl_5)

Alcohols (ROH) react with phosphorous pentachloride to yield alkyl chlorides (RX).

$$ROH + PCl_5 \longrightarrow R\text{-}Cl + POCl_3 + HCl$$

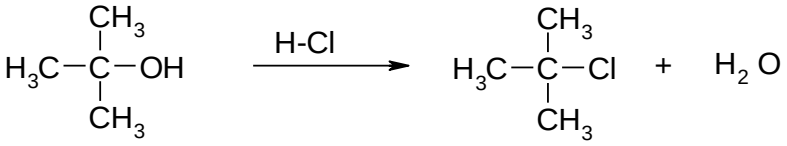
$$CH_3CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + POCl_3 + H\text{-}Cl$$

2. Alcohols to Alkyl halides

Alcohols can be converted to alkyl halides by treatment of either HCl, HBr at 0°C. Primary and secondary alcohols are little resistant to acids because the –OH hydrogen is slightly acidic in nature. This conversion can be best achieved by treatment of alcohols with $SOCl_2$ or PBr_3.

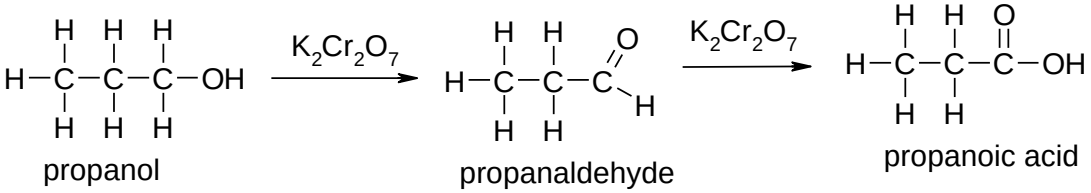
$$CH_3CH_2CH_2OH \xrightarrow{SOCl_2} CH_3CH_2CH_2Cl + H\text{-}Cl + SO_2$$

$$CH_3CH_2OH \xrightarrow{PBr_3} CH_3CH_2Br + HOPBr_2$$



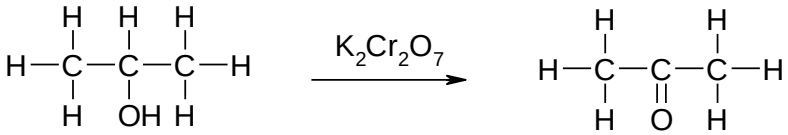
3. Oxidation of Alcohols:

Primary and secondary alcohols are readily oxidizes by a variety of oxidants such as acidified dichromate (VI) and acidic or alkaline potassium permanganate (VII). The product formed from this reaction contains a carbonyl compound (there is (C=O bond instead of C-OH bond).



propanol propanaldehyde propanoic acid

In case of primary alcohols, an aldehyde is initially formed which is further oxidised to carboxylic acids. When a secondary alcohol is oxidised, a ketone is formed and cannot be further oxidised.

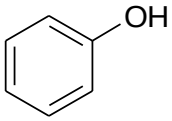


2-propanol 2-propanone

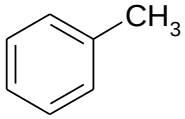
However, tertiary alcohols cannot be oxidised since there is no hydrogens to be removed from the carbon with OH group.

PHENOLS

Phenols are aromatic alcohol and has higher boiling points compared to toluene as it can also form hydrogen bonds in liquid state. Phenols also has both weakly acidic and weakly basic characteristics.



phenol

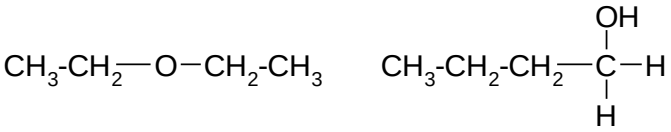


toluene

ETHERS

Ethers are a group of compounds containing oxygen. The oxygen in the compound is bonded to two alkyl groups (two carbon atoms). Ether is **symmetrical** if both alkyl groups attached are same, for example Diethylether: $CH_3CH_2OCH_2CH_3$. If the ether has two different alkyl groups attached then it is **unsymmetrical**. For example ethylmethylether: $CH_3OCH_2CH_3$.

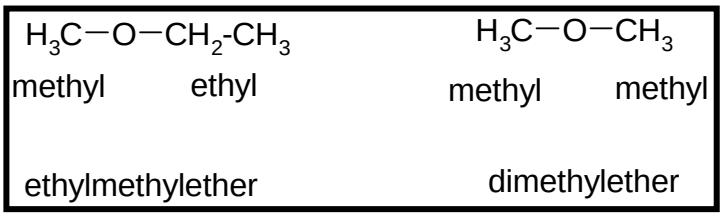
Ethers have the same molecular formula of the corresponding alcohol. For instance, diethylether has 4 carbon atoms and therefore has the molecular formula of $C_4H_{10}O$, which is same as that of butanol (4 carbon atoms in the molecule).



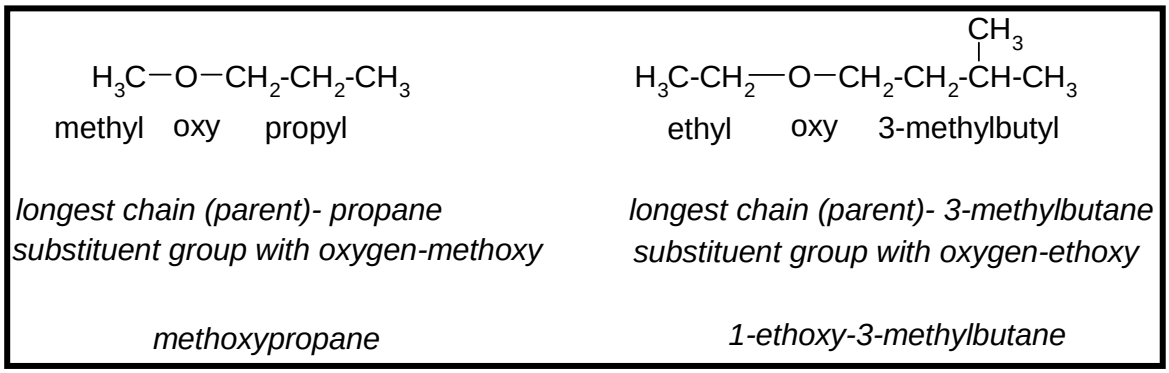
diethylether butanol

NOMENCLATURE OF ETHERS

Ethers are given common names, by naming the both the alkyl groups attached to the oxygen. The names of the alkyl groups are arranged alphabetically, and the word ether is added at the end. For the symmetrical ethers, the prefix "di" is added to the name of the alkyl group attached.

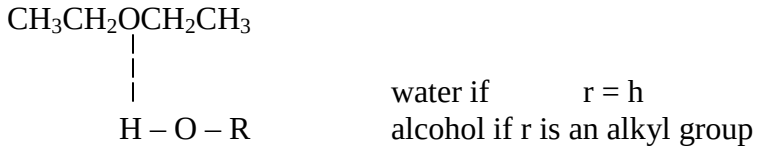


In the IUPAC system ethers are named as alkoxyhydrocarbons. The longest chain becomes the parent hydrocarbon chain, and the remaining –OR group is named as substituent called alkoxy (alkyl group and the oxy group).



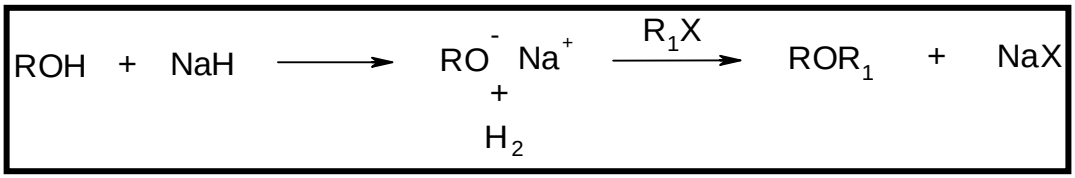
PROPERTIES OF ETHERS

Ethers cannot form intermolecular hydrogen bonds because they have no hydrogen attached to oxygen. However, ethers that have less than 6 carbon atoms in the molecule can form hydrogen bonds with water or alcohols. Ethers that have 6 or more carbon atoms in the molecule cannot form hydrogen bonds with water because the nonpolar alkyl group is too large to dissolve in water. Nevertheless, ethers of any size are soluble in organic solvents.



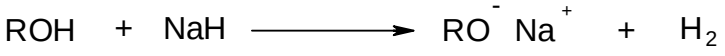
PREPARATION OF ETHERS

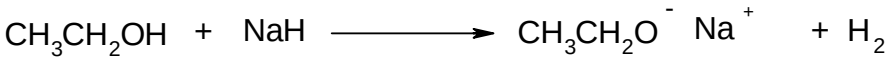
A general method to prepare ethers from alcohols is as follows:



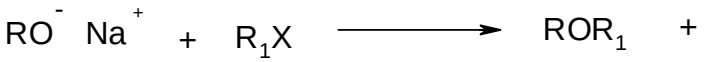
The reaction is carried out in two steps.

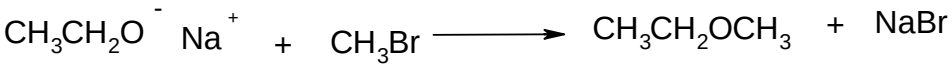
Step 1: Reaction of sodium hydride with alcohol. This Brønsted Lowry Acid-base Reaction will produce sodium alkoxide (RONa).



e.g 

Step 2: substitution of the halogen in alkyl halide R_1X by the nucleophile RO^-: alkoxide produced in step 1.

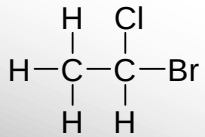


e.g 

This is a versatile laboratory procedure for synthesizing ethers.

Did You Know…?

+ Diethylether was used as an anesthetic in surgery during 19th century because it was safe, easy to administer and caused little patient mortality. It is now replaced by halothane (CH_3-CHClBr) because diethylether is highly flammable and causes nausia in many patients.



Structure of halothane

ALKYL HALIDES

General formula: RX

PHYSICAL PROPERTIES

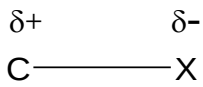
Alkyl halides have very low solubility in water, but are more miscible with other relatively non-polar solvents.

Methyl iodide, CH_3I, (BP=42°C) is the only monohalomethane that is liquid at room temperature and atmospheric pressure. Ethyl bromide, CH_3CH_2Br, (BP=38°C) and ethyl iodide, CH_3CH_2I (BP=72°C) are both liquids but ethyl chloride, CH_3CH_2Cl, (BP=12°C) is a gas. In general alkyl chloride and iodides tend to have low boiling points near those of alkanes of similar molecular weights.

NATURE OF CARBON HALOGEN BONDS

The polarity of the carbon-halogen bond makes the carbon atom susceptible to attack by a nucleophile. A nucleophile is a neutral molecules or negative ion that has an unshared pair of electrons which can be donated to the bond formation with the positive centre. This reaction is called **nucleophilic substitution** reation.

Positive centre that forms a bond with the nucleophile

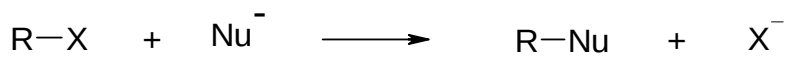


The electronegative halogen polarises the C-X bond

δ+	slightly positive
δ-	slightly negative

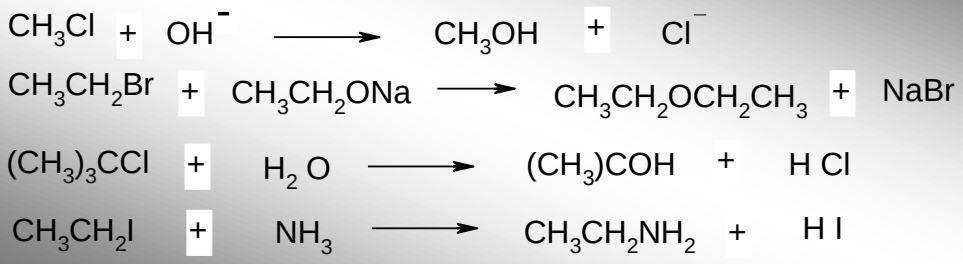
NUCLEOPHILIC SUBSTITUTION REACTIONS

There are many reactions of the general type shown below.



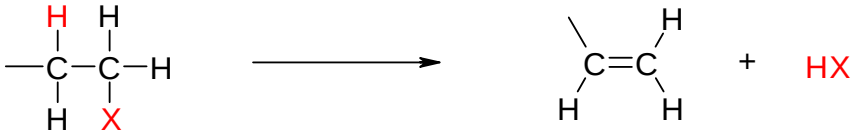
In this type of reaction a nucleophile reacts with an alkyl halide by replacing the halogen substituent. A substitution reaction takes place, and the halogen substituent leaves as a halide ion. This reaction is called a nucleophile substitution reaction because the substitution reaction is initiated by a nucleophile. A nucleophile is a specie that has a lone pair of electrons or excess of electrons (negative charge).

Examples:

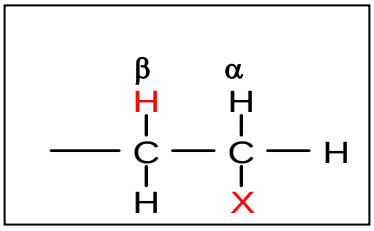


ELIMINATION REACTION

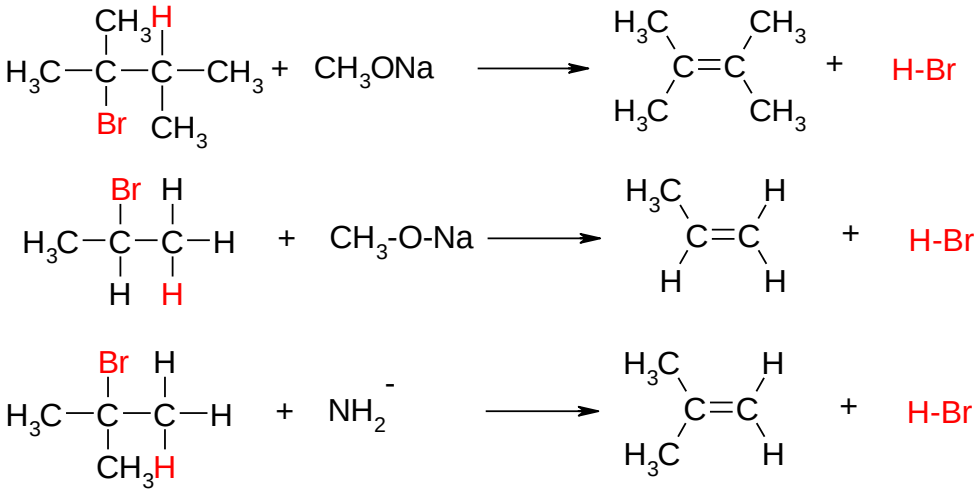
In an elimination reaction, a hydrogen atom and the halogen atom of the alkyl halide molecule is removed (eliminated) from the adjacent atoms of the reactant. This leads to introduction of a multiple bond (double bond). This reaction is also called dehydrohalogenation as it involves elimination of HX from adjacent atoms of an alkyl halide. This reaction is initiated in presence of a strong base (or a nucleophile).



Carbon that bears the halogen is called the alpha (α) carbon and any carbon adjacent to it a beta (β) carbon. Hydrogen that is eliminated during dehydrohalogenation is a beta (β) hydrogen (a hydrogen attached to β carbon is called β hydrogen).



Some elimination reactions are:



SUBSTITUTION VERSUS ELIMINATION

Since the relative part of a nucleophile or a base is unshared electron pairs of all nucleophiles are potential bases and all bases are potential nucleophiles. Nucleophilic substitution reactions and elimination reactions often compete with each other.

The path that a reaction follows depends on the nature of both alkyl halide and the nucleophile. The table below gives the most important reaction according to the nature of alkyl halide.

CH_3X	**RCH_2X**	**R_2CHX**	**R_3CX**
Methyl halide **Primary alkyl halide**	**Primary alkyl halide**	**Secondary alkyl halide**	**Tertiary alkyl halide**
Nucleophilic Mainly substitution	Weak base- substitution	Weak base Substitution	strongly hindered Strong base- elimination

Relative strengths of nucleophiles are:

$RO^- > HO^- > RCOO^-$; $I^- > Br^- > Cl^- > F^-$

AMINES

Amines are organic bases. They are derived from ammonia by replacing the hydrogen (s) with the alkyl groups.

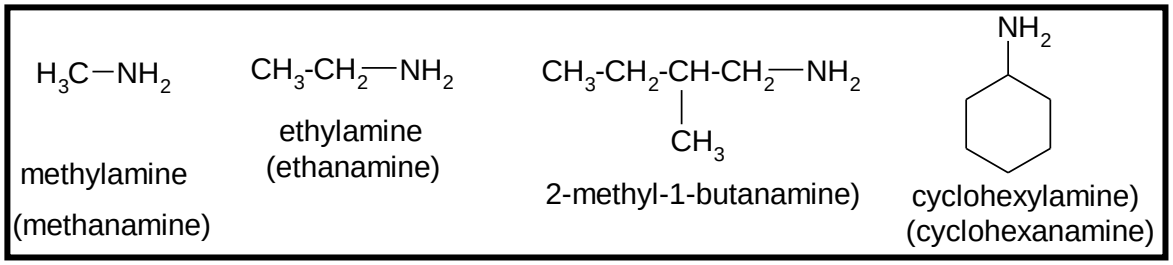
CLASSIFICATION OF AMINES

Classification	Structure	Example	Name
Primary Amine	$R\text{-}NH_2$	$CH_3\text{-}CH_2\text{-}NH_2$	ethyl amine
Secondary Amine	$R_2\text{-}NH$	$CH_3\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_3$	diethylamine
Tertiary Amine	$R_3\text{-}N$	$(CH_3)_3\text{-}N$	trimethylamine

NOMENCLATURE

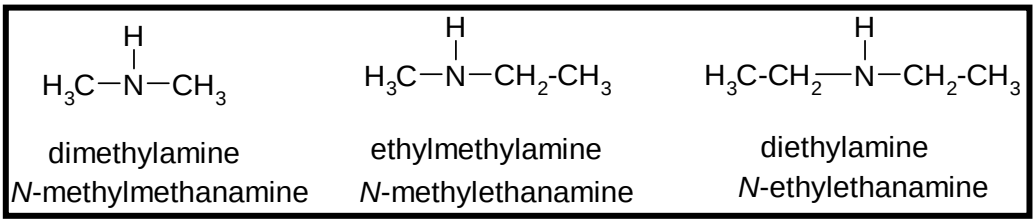
In common nomenclature most primary amines are names as *alkylamines*. In systematic nomenclature, the name of the alkyl group is added to the suffix *–amine*.

Primary Amines

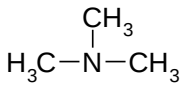
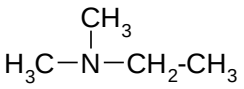
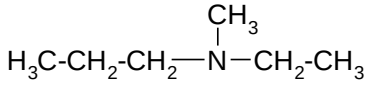


Most secondary and tertiary amines are named in the same way as the primary amines. In common nomenclature, individual groups are designated individually if the groups are different, but if the groups are same, then the prefix di- or tri- is used. However, in systematic nomenclature, *N* is used to designate the substitutents attached to a nitrogen atom.

Secondary Amines



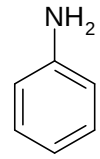
Tertiary Amines

		
trimethylamine	ethyldimethylamine	ethylmethylpropylamine
N, N-dimethylmethanamine	*N, N*-dimethylethanamine	*N*-methyl-*N*-ethylpropanamine

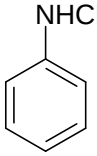
If the compound has other functional groups present, then the-NH_2 is called the amino group.

NH_2-CH_2-CH_2-OH	NH_2-CH_2-CH_2-COOH
2-aminoethanol	3-aminopropanoic acid

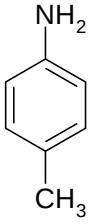
The common aromatic amines are:



Aniline



N-methylaniline

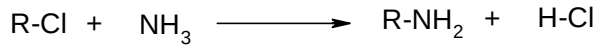


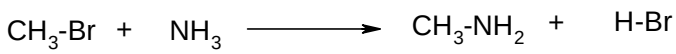
p-aminotoluene

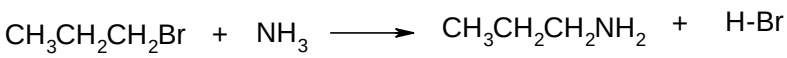
PREPARATION OF PRIMARY AMINES

There are many ways of preparing amines. Some of the methods are listed below.

1. Nucleophilic substitution reaction of alkyl halides with ammonia.

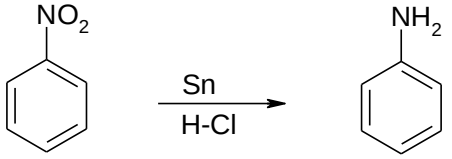






This reaction has limitations because multiple alkylation occurs in which a mixture of primary, secondary and tertiary amines will be synthesised.

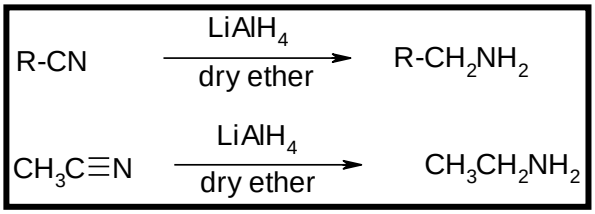
2. Reduction of Nitro groups



This method is normally employed for the preparation of aromatic amines in which the nitro group is reduced (removal of oxygen) in presence of a catalyst in acid medium.

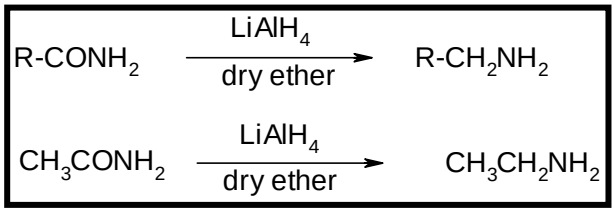
3. Reduction of Nitriles

Primary amines are produced by the reduction of nitriles using a very powerful reducing agent such as lithium tetrahydridoaluminate ($LiAlH_4$) in presence of dry ether.



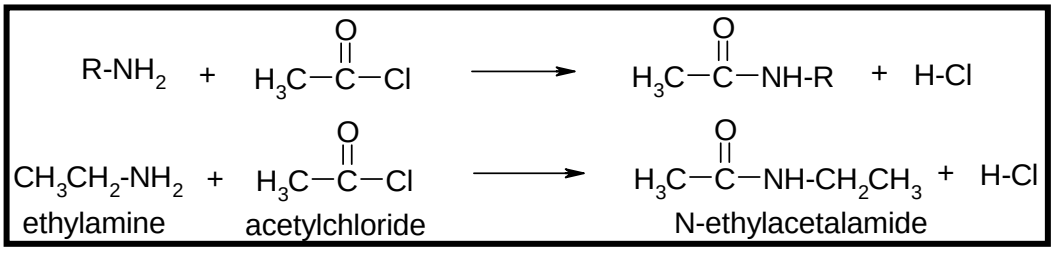
4. Reduction of Amides

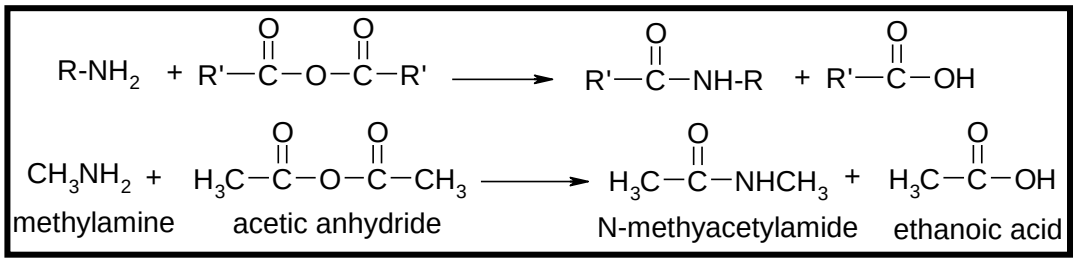
Amides (like nitriles) can be reduced by lithium tetrahydridoaluminate ($LiAlH_4$).



5. Reactions of Amines with acid chlorides and acid anhydrides

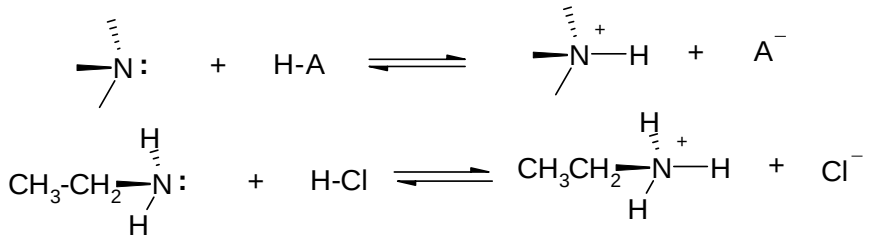
Acid chlorides and acid anhydrides act as electrophile and -NH_2 group as a nucleophile. These reactions produce **amides**, a group of organic compounds that contain C=O and N bonded to each other.





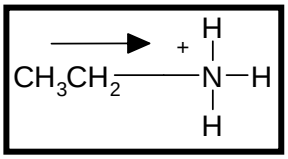
Amines as Bases

The chemistry of amines is centered around the lone pair of electrons on nitrogen. This is because the lone pair of electrons is both nucleophilic and basic. When amines reacts with acid to form acid-base salts as in the equation below. The salt formed in this case is ethylammonium chloride. Treating the ethylammonium chloride salt with a strong base like NaOH can reverse this reaction.



Amines are stronger bases than ammonia, alcohol, ether and water. To understand the strength of amines, let's study the following reactions.

The strength of the base depends on the stability of the cation formed when the nitrogen's lone pair of electrons is used to form the bond with the proton. The difference between the two equations is the presence of CH_3CH_2 - group in the second equation. Remember that alkyl groups donate electron density inductively towards the positive charge.



The CH_3CH_2 – group pushes electrons towards the $-NH_3^+$ group. This effect stabilizes the positive charge on the nitrogen, as the strength of the positive charge is reduced. The result is $CH_3CH_2\ NH_3^+$ which is more stable and therefore $CH_3CH_2\ NH_2$ is a stronger base.

$$NH_3\,(aq) + H^+(aq) \rightleftharpoons NH_4^+(aq)$$

$$CH_3CH_2NH_2\,(aq) + H^+(aq) \rightleftharpoons CH_3CH_2NH_3^+(aq)$$

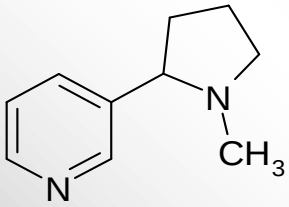
The strength of amines can also be determined by the K_b values. The higher the K_b values, the stronger is the base. The K_b values of some amines are given in the table 5.7 below.

Table 5.7: Relative strengths of Amines

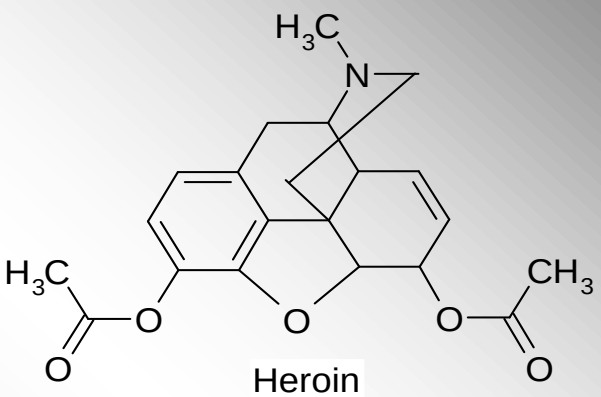
Formula	**Name**	K_b **at 25°C/mol dm^3**
NH_3	Ammonia	$1.8X10^{-5}$
$CH_3CH_2NH_2$	Ethylamine	$5.4X10^{-4}$
$(CH_3CH_2)_2NH$	Diethylamine	$1.3X10^{-3}$
$C_6H_5NH_2$	Phenylamine (aniline)	$5.0X10^{-10}$

Did You Know…?

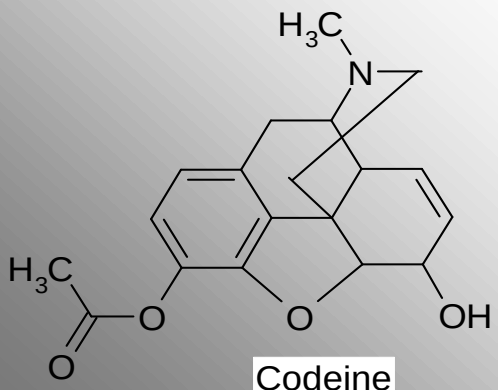
Some of the well known drugs such as morphine, heroin, codeine and nicotine are amines



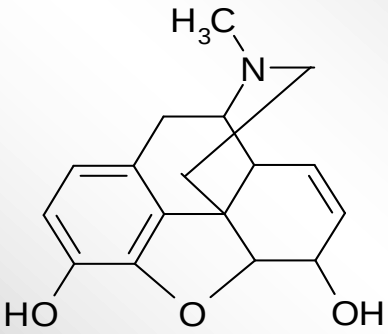
Nicotine



Heroin



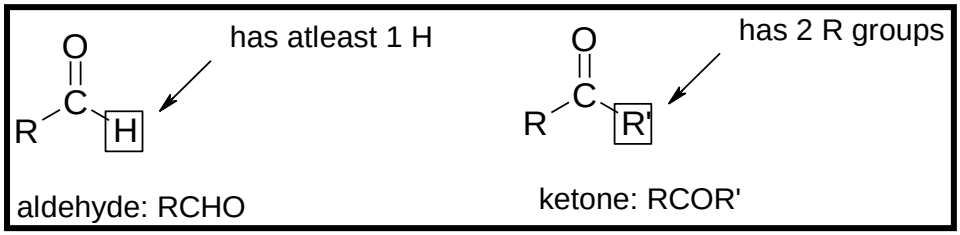
Codeine



Morphine

ALDEHYDES AND KETONES

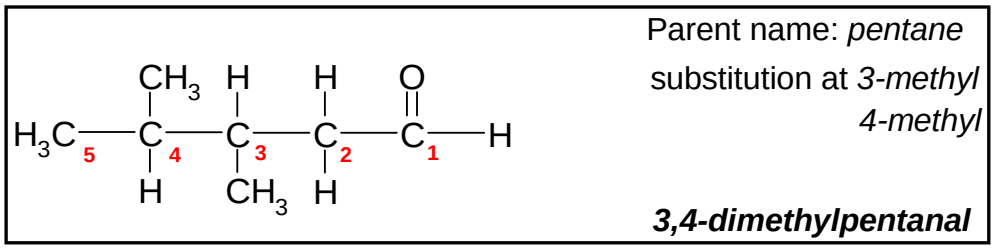
Aldehydes and ketones are a group of compounds that contain carbon and hydrogen atoms bonded to the carbonyl group (C=O). An aldehyde has at least one hydrogen atom attached to the carbonyl carbon whereas a ketone has two alkyl (or aryl) groups attached to the carbonyl carbon.



NAMING ALDEHYDES

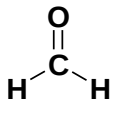
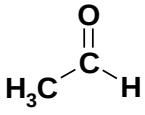
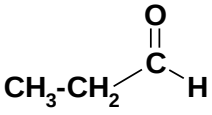
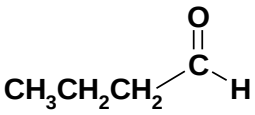
In the IUPAC nomenclature, aliphatic aldehydes are named by replacing the terminal **"e"** of the longest chain alkane by the suffix ***"al"***. The carbon number one is always the carbon with the carbonyl group. All other usual rules of nomenclature apply.

For example:



Many aldehydes have common names that are widely used. These names are derived from the names of common carboxylic acids (which describe where the acid was found). The common name of an aldehyde is given by adding the parent name to the suffix-aldehyde. Some common aldehydes are given in the table 5.8 below.

Table: 5.8: Some common aldehydes

Structure				
Common Name	formaldehyde	acetaldehyde	propionaldehyde	butyraldehyde
IUPAC name	methanal	ethanal	propanal	butanal

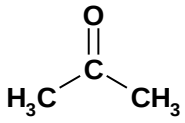
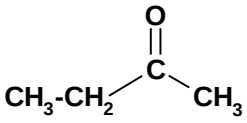
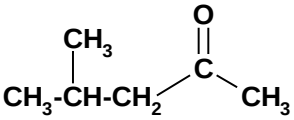
NAMING KETONES

Ketones can be identified with suffix-***"one"*** in the name. To name the ketones:

1. Find the longest chain containing the carbonyl group.
2. Change the **–e** ending of the parent alkane to **–one**.
3. Number the carbon chain to give the carbonyl carbon the lowest position.
4. Apply all other usual rules of nomenclature.

Some common ketones are given in table 5.9 below.

Table 5.9: Some common ketones

Structure			
Common Name	acetone	ethylmethylketone	methyl-*iso*-butylketone
IUPAC name	propanone	2-butanone	2-methylpentanone

Both aldehydes and ketones have the general formula $C_nH_{2n}O$. Note that as in alkene the presence of double bond replaces two hydrogens from the carbon.

PHYSICAL PROPERTIES

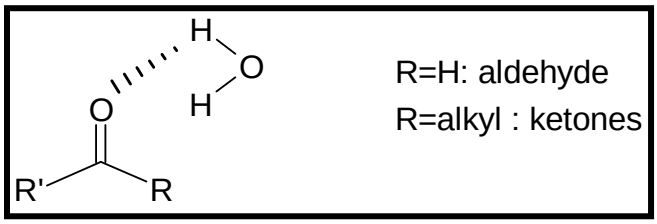
Aldehydes and ketones exhibit dipole-dipole interaction, because of the polar carbonyl group, hence their boiling point is higher than the corresponding alkane (alkanes with similar molecular mass). Both aldehydes and ketones are not capable of forming intermolecular hydrogen bonding due to the absence of the O-H bond, making them less polar than alcohols and carboxylic acids. Aldehydes and ketones will therefore have lower boiling point than correspoding alcohols and carboxylic acids.

Table 5.10 gives the boiling points and solubilities in water of some simple aldehydes and ketones:

Table 5.10: Physical Properties of Some Aldehydes and Ketones

Aldehydes	**Structure**	**Boiling point ^{0}C**	**Solubility in water**
Methanal (formaldehyde)	HCHO	-21	very soluble
Ethanal (acetaldehyde)	CH_3CHO	20	very soluble
propanal	CH_3CH_2CHO	49	16g/100cm^3
Ketones			
Propanone (acetone)	CH_3COCH_3	56	very soluble
2-butanone (methylethyl ketone)	$CH_3COCH_2CH_3$	80	26/100cm^3

Although aldehydes and ketones cannot form intermolecular hydrogen bonds, they will form hydrogen bond with water and alcohol molecules.



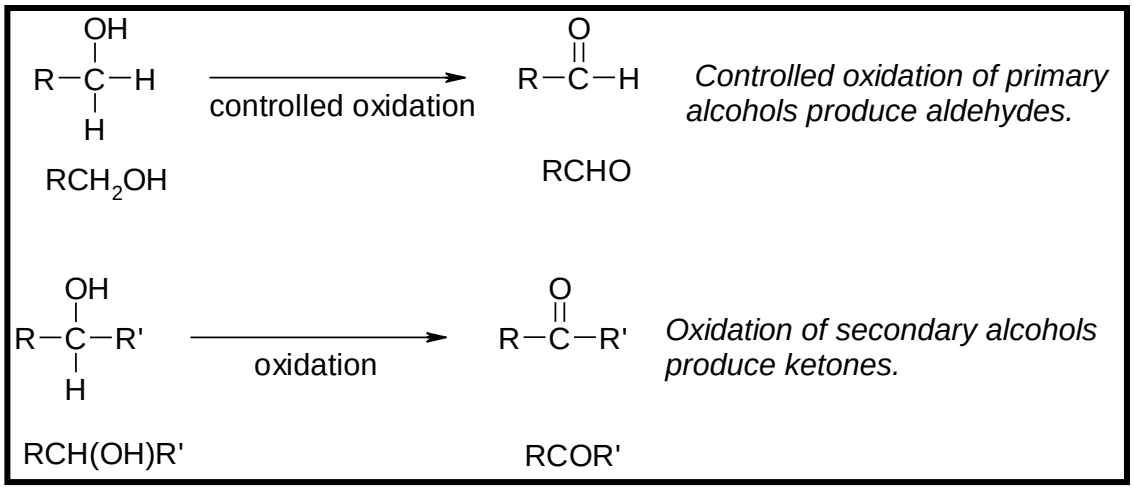
General Observations for aldehydes, RCHO and ketones, RCOR:

- Increasing strength of intermolecular forces increases the boiling point.

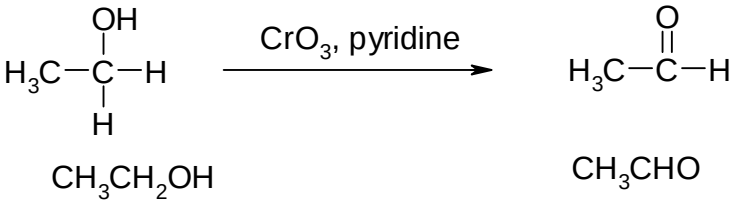
- RCHO and RCOR are soluble in all organic solvent regardless of size.
- RCHO and RCOR having less than 6 carbon are soluble in water and form H-bonds.
- RCHO and RCOR having 6 or more carbons are insoluble in water because of nonpolar R group.

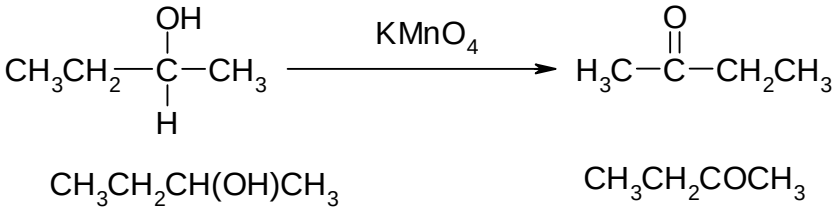
PREPARATION

Aldehydes and ketones are prepared by the oxidation of alcohols as follows:



Examples:





Any oxidizing agents such as $K_2Cr_2O_7$, $KMnO_4$, CrO_3 or Ozone-O_3) can be used to convert alcohols to ketones or carboxylic acids. However, if you want the reaction to stop at aldehydes, then a reductive agent such as pyridine should be used.

REACTION OF ALDEHYDES AND KETONES

1. With Tollens Reagent

Tollens Reagent is a mixture of alkaline ammonium hydroxide (NH_4OH) solution and silver nitrate which forms a silver-ammonia complex cation, $Ag(NH_3)_2^+$. Aldehydes undergo oxidation in the presence of this cation in the following manner:

$$RCHO + Ag(NH_3)_2^+ \longrightarrow RCOO^- + Ag\downarrow$$

Silver precipitates as shown in the equation and deposits to give a silver mirror on the walls of the test tube. This reaction is sometimes referred to as the **silver mirror test**, for aldehydes.

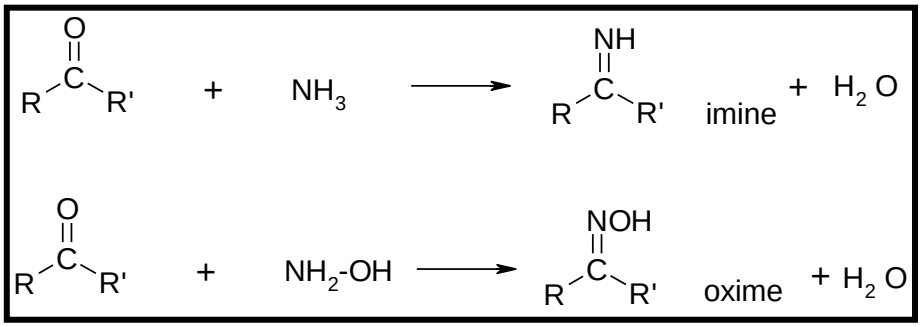
2. With Fehlings Reagent

Fehlings reagent contains a deep blue cupric tartarate complex. Most aldehydes reduce the cupric ion to the cuprous ion, which then gives the red colored precipitate of cuprous oxide. Hence this reagent is also used as a test for aldehydes. During this process the aldehyde gets oxidized to the carboxylic acid.

$$RCHO + 2Cu^{2+} + 4OH^- \longrightarrow \underset{\text{Red ppt}}{Cu_2O\ (s)} + RCOO^- + 2H_2O$$

3. With Ammonia and Hydroxylamine

Aldehydes and ketones react with reagents such as ammonia and hydroxylamine by removing a molecule of water (2 H's from N and O from carbonyl). Elimination of water gives an imine with ammonia and an oxime with hydroxylamine as shown below.



If R,R' = alkyl , then it's a ketone,
If R= H; R' = alkyl, then its an aldehyde.

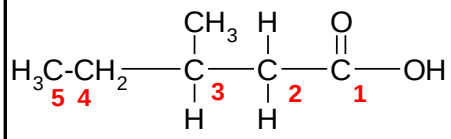
CARBOXYLIC ACIDS

Carboxylic acids are a group of compounds that have a general formula RCOOH. It has two functional groups, a carbonyl (C=O) and a alcohol group (OH) on the terminal carbon.

NOMENCLATURE

1. Count the longest continuous chain including the carbon with COOH group.
2. Number the chain starting the carbon with COOH.
3. Give the name of the corresponding alkane ad replace the –e ending to –oic acid.
4. Identify the substituents and list them in alphabetical order.

For Example:

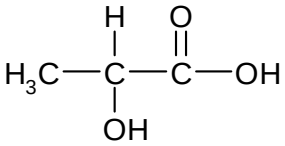
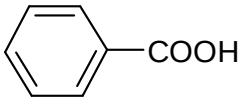


parent name: pentane
substituent: @3-methyl

3-methypentanioc acid

Some Common acids are listed in the table 5.11 below.

Table 5.11: Common Carboxylic acids

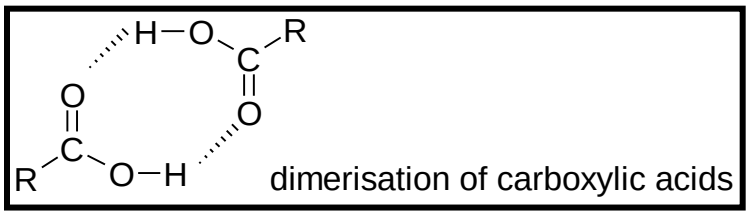
Structural Formula	IUPAC name	Common Name
HCOOH	methanoic acid	formic acid
CH_3COOH	ethanoic acid	acetic acid
	2-hydroxypropanoic acid	lactic acid
	benzenecarboxylic acid	benzoic acid

PHYSICAL PROPERTIES

The melting and the boiling points of carboxylic acids are higher than the comparative (with similar Mr) hydrocarbons and alcohols indicate strong intermolecular forces.

Compound	**Name**	**Molecular Mass (g/mol)**	**Boiling Point (°C)**
CH_2-CH_2-C(CH_3)=CH_2	2-methyl –1-butene	71.1	-6.3
CH_2-CH_2-CO-CH_3	2-butanone	72.1	80
CH_2-CH_2-CH (OH)-CH_3	2-butanol	74.1	99
CH_2-CH_2-COOH	Propanoic acid	74.1	141

There is unique intermolecular hydrogen bonding that contributes to the attractive forces. The OH group of one acid donates the proton to the carbonyl group of the other acid as described by the diagram below.



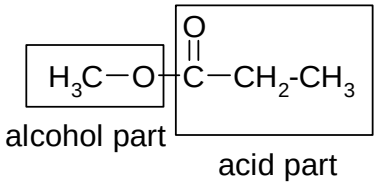
dimerisation of carboxylic acids

ESTERS – DERIVATIVES OF CARBOXYLIC ACIDS

Carboxylic acid (RCO_2H) reacts with alcohols in the presence of acids to give esters. Esters are therefore derivatives of these acids. They can be formulated as RCO_2R', where R' can be alkyl or aryl groups and R can be H, alkyl or aryl groups.

IUPAC names of esters are derived from the names of alcohol part (with ending "**yl**") and the acid part (with ending "**oate**"). The alcohol part of the ester is written first and then the acid part.

Example 1:

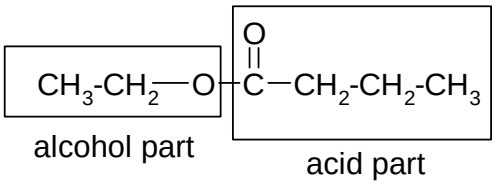


alcohol part: methyl

acid part: propanoic acid

name: methyl propanoate

Example 2:



alcohol part: ethyl

acid part: butanoic acid

name: ethyl butanoate

Most esters have pleasant odors. Many have distinct **fruity smells**. This characteristic is sometimes used as a test for organic acids. If the compound is reacted with alcohols in presence of an acid, and it gives a fruity smell, then it is an organic acid

Table 5.12 gives the names and structures of some esters and their boiling points.

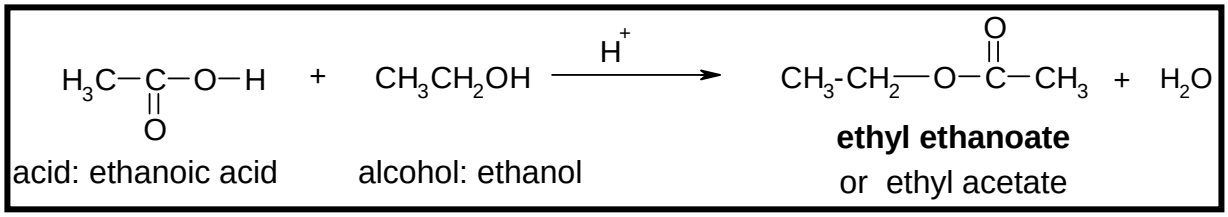
Table 5.12: Names, Structures, Odors & Boiling Points of Some Esters

Name	**Structure**	**Odor**	**Boiling Point (°C)**
Methyl ethanoate/ Methyl acetate	$CH_3CO_2CH_3$	pleasant	57
Ethyl ethanoate	$CH_3CO_2CH_2CH_3$	pleasant	77
Ethyl butanoate	$CH_3(CH_2)CO_2CH_2CH_3$	pineapple	121
3-Methylbutyl ethanoate	$CH_3CO_2(CH_2)CH(CH_3)_2$	banana	142

PREPARATION OF ESTERS

1. Reaction of alcohol with carboxylic acids

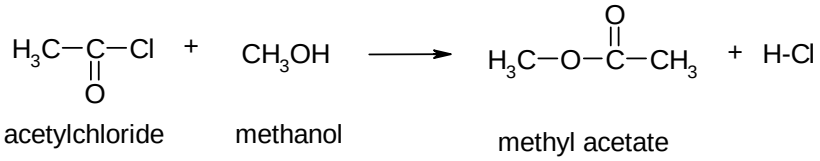
Simple esters are best prepared by reacting the corresponding alcohol ($R^{'}OH$) and the carboxylic acid (RCOOH) in the presence of small amounts of concentrated H_2SO_4. H_2SO_4 removes the water formed in the above equilibrium reaction and drives the reaction in the forward direction.



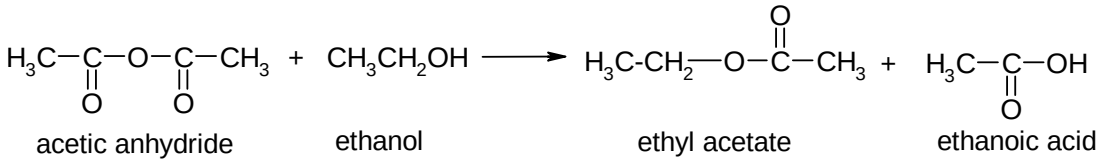
2. Reaction of alcohols with acid anhydride

Esters can also be prepared by the reaction of alcohols with **acid chlorides** and **acetic anhydride.**

Reaction with acid chloride



Reaction with acetic anhydride



REACTIONS OF ESTERS

1. With water

Esters ($R_1CO_2R_2$) are formed from carboxylic acids reacting with alcohols in the presence of concentrated sulphuric acid. This reaction is called **esterification**. The reverse reaction of esterification is called **hydrolysis** of ester. During hydrolysis, esters break to form parent acid (R_1CO_2H) and alcohol R_2OH:

$$R_1COOR_2 + OH_2 \underset{}{\overset{H^+}{\rightleftharpoons}} R_1COOH + R_2OH$$

Esters can also be hydrolysed with a strong base such as NaOH as shown below:

$$R_1COOR_2 + OH_2 \longrightarrow R_1COOH + R_2OH$$

The above reaction is also called the **saponification reaction** since soaps, which are sodium salts of some carboxylic acids, are produced this way. This is discussed later in the chapter.

2. With alcohols

With an alcohol (ROH), ester undergoes a **trans-esterification** reaction:

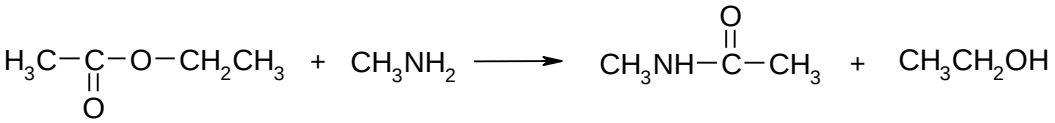
$$R_1COOR_2 + \underset{\text{excess}}{ROH} \overset{H^+}{\rightleftharpoons} R_1COOR + R_2OH$$

The reaction is catalysed by conc. H_2SO_4 and is an equilibrium reaction. To drive the reaction forward, an excess alcohol ROH should be used.

3. With Ammonia

Esters react with aqueous ammonia or amines to yield acid amides:

$$R_1COOR_2 + RNH_2 \longrightarrow R_1CONHR + R_2OH$$

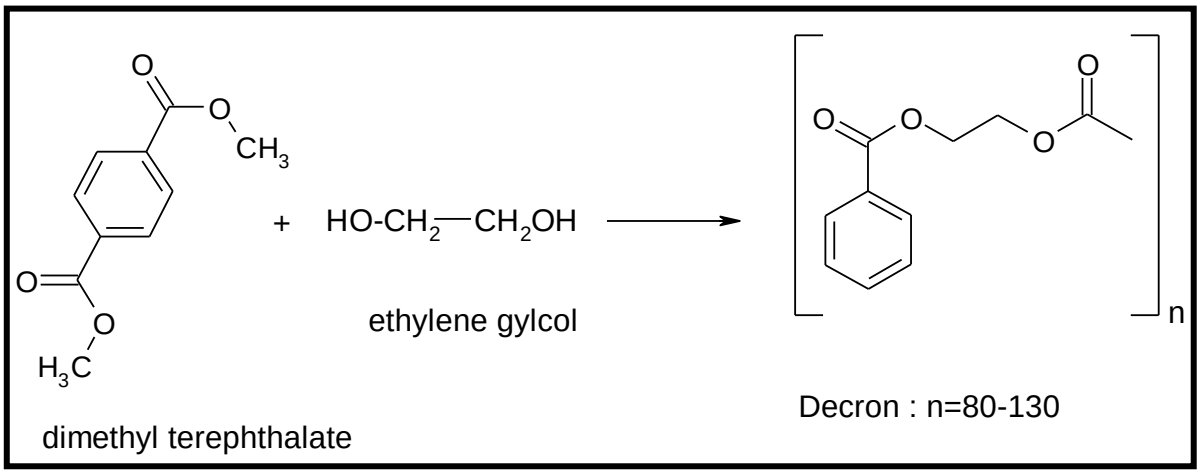


ethyl acetate methyamine N-methylacetamide ethanol

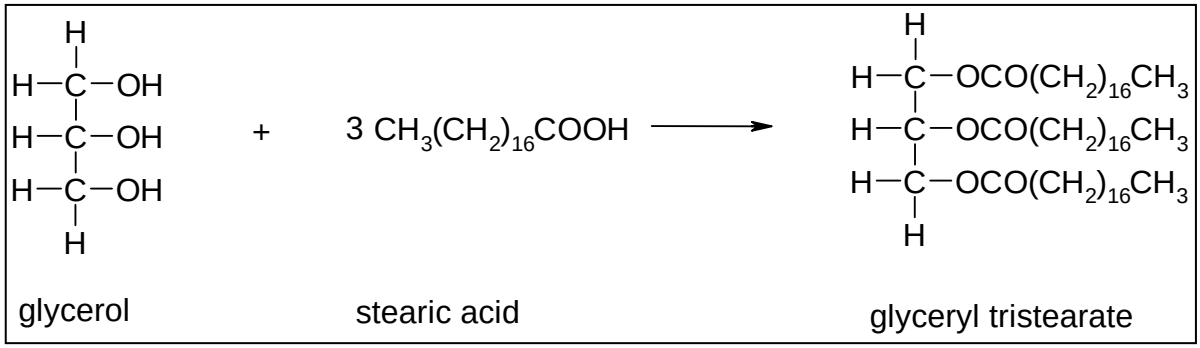
USEFUL ESTERS

Some esters have odors that resemble foods such as pineapple and banana (table 5.12) These flavor substances can be synthesised by using the method to prepare esters and are used as of artificial food flavours.

The synthetic fibre called **Dacron** is polyester formed from the trans-esterification of **dimethyl terephthalate** and the alcohol **ethylene glycol**. Dacron is an example of a linear polyer and makes an excellent fibre with can be spun to produce textiles. Dacron is polyester as it has several ester groups ($-CO_2-$).



Another commercially useful ester is the vegetable fat or oil. Vegetable oils are esters with glycerol and unsaturated acids. An example of fat is **glycerol tristearate**, which is formed from the alcohol glycerol, and the carboxylic acid called stearic acid.



Hydrolysis of an ester such as glyceryl tristearate with NaOH produces soap and the reaction is called **saponification reaction.**

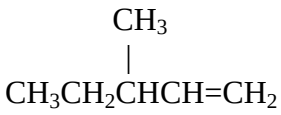
$$\text{Glyceryl tristearate} + \text{NaOH} \xrightarrow[\text{Heat}]{H_2O} \text{glycerol} + CH_3(CH_2)_{16}COONa$$

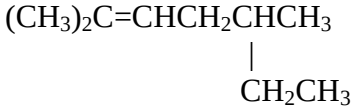
sodium stearate (a soap)

5.1 Nomenclature

Questions:

1) Name the following compounds:

(a) 

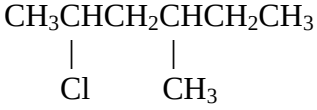
(b) 

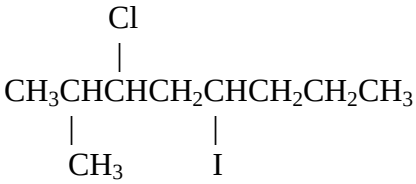
2) Write the structures corresponding to the following names:

(a) 2,3-Dimethyl-2-pentene
(b) 3,7,7-Trimethyl-4-octene
(c) 3-methyl-2-heptene
(d) 2,2-dimethyl-3-hexene

3) Name these compounds:

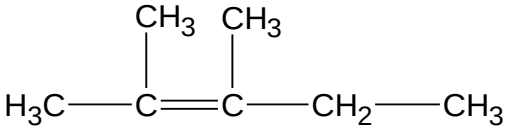
(a) $CH_3CH_2CH_2CH_2CH_2Br$

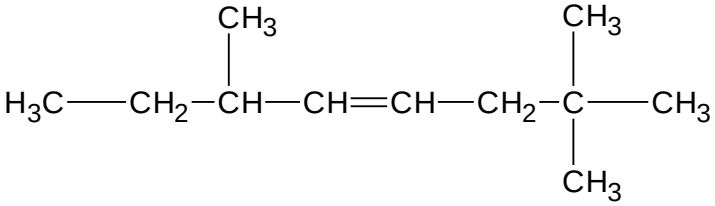
(b) 

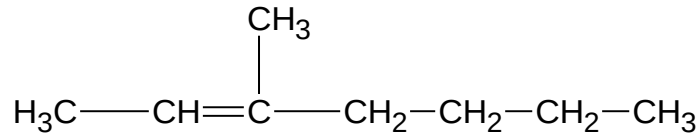
(c) 

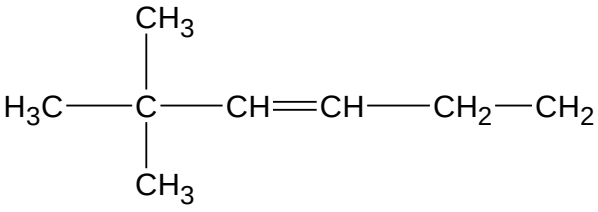
Answers:

1) (a) 2-methylprop-1-ene
(b) 2,5-dimethylhept-2-ene

2) (a) 

(b) 

(c) 

(d) 

3) (a) Bromopentane
(b) 2-chloro-4-methylhexane
(d) 3-chloro-5-ido-2-methyloctane

5.2 Isomerism

Questions:

1) Assign priorities to the groups in each set:
(a) $–CH_2OH$ and $–CH_2CH_2OH$
(b) $–CH_2OH$ and $–CH=CH_2$
(c) $–CH_2OH$ and $C(CH_3)_3$
(d) $–H$, $-CH_3$, $-OH$, $-CH_2OH$
(e) $–CH_2CH=CH_2$, $-CH=Ch_2$, $-CH_3$, $-CH_2CO_2H$

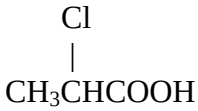
2) How many isomers exist of 3-methylcyclopentanol?

3) Write all the structural isomers for the each of the following
(a) C_3H_8O (b) $C_4H_8O_2$ (acids and esters)

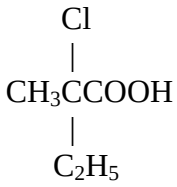
(c) $C_4H_{11}N$ (d) C_4H_9X

4) For which of the following compounds is cis-trans isomerism possible? Where cis-trans isomerism is possible, write the structural formulas for the isomeric compounds.
a) 1-Butene
b) 1-chloro-1-butene
c) 2-Methylpropene
d) 1,1-Dichloropropene
e) 2-heptene
f) 2-Methyl-2-heptene

5) Consider the following structures. Identify the carbon atoms in the molecules below which are asymmetric (chiral).

a) 

b) H_3CCH_2Cl

c) 

d) $CH_3CH_2CH_2CH_3$

e) $CH_3CH(COOH)CH_2CH_3$

f) $CH_3CH_2CH_3$

g) $(CH_3)_3C\text{-}CH(CH_3)COOH$

h) CH_3CHCl_2

i) $(CH_3)_3CH(OH)CH_3$

j) $CH_3CH_2C(CH_3)_2OH$

6) Consider the following pairs of structures. Identify the relationship between them by describing them as representing enantiomers, structural isomers, geometrical isomers or two molecules of the same compound:

a) 

b) 

c) 

d) 

e) $CH_3C{=}CCH_3$ (H, H) $\qquad$ $CH_3C{=}CCH_3$ (H, H)

f) $CH_3CH{=}CCl_2$ $\qquad$ $CH_3C(Cl){=}CHCl$

g) $CH_3C{=}C{-}CH_3$ (Cl, H) $\qquad$ $CH_3C(H){=}CCH_3$ (Cl)

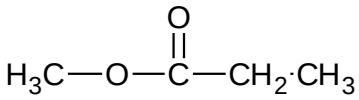
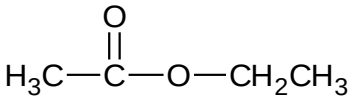
h) $CH_3C(=O)OCH_3$ $\qquad$ $CH_3CH_2C(=O)OH$

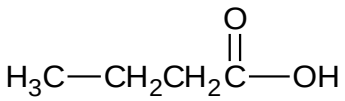
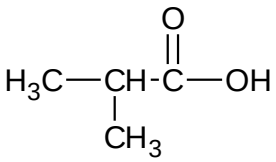
Answers:

1) (a) $-CH_2OH$ and $-CH_2CH_2OH$
1 **2**
(b) $-CH_2OH$ and $-CH{=}CH_2$
1 **2**
(c) $-CH_2OH$ and $C(CH_3)_3$
1 **2**
(d) $-H$, $-CH_3$, $-OH$, $-CH_2OH$
4 **3** **1** **2**
(e) $-CH_2CH{=}CH_2$, $-CH{=}CH_2$, $-CH_3$, $-CH_2CO_2H$
3 **2** **4** **1**

2) 4 isomers. The *cis* isomer has 2 enantiomers and the *trans* isomer has 2 enantiomers.

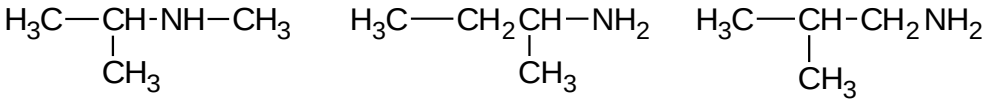
3) (a) $CH_3OCH_2CH_3$, $CH_3CH_2CH_2OH$, $CH_3CH(OH)CH_3$

(b)  

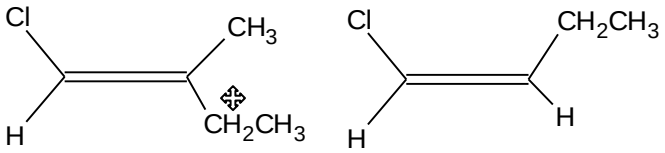
(c) $CH_3CH_2CH_2CH_2NH_2$, $(CH_3)_3CNH_2$, $CH_3CH_2CH_2NHCH_3$,

$CH_3CH_2NHCH_2CH_3$, $CH_3CH_2N(CH_3)_2$,

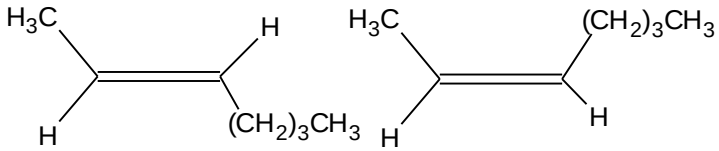


(d) $CH_3CH_2CH_2CH_2X$, $CH_3CH_2CHXCH_3$, $(CH_3)_3CHX$, $(CH_3)_2CHCH_2X$

4) (a) Not Possible

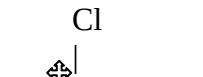
(b) Possible 

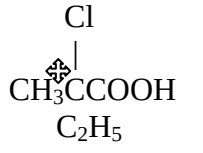
(c) Not Possible (d) Not Possible

(e)Possible 

(f) Not Possible

5)

a)  b) Achiral

c)  d) Achiral

e)  f) Achiral

g) Achiral h) Achiral

i)  j) Achiral

6) (a) Enantiomers (optical isomers) (b) same compound
(c) Structural isomers (d) same compound
(d) same compound (e) structural isomers
(f) geometrical isomers (h) structural isomers

5.3.2 Alkanes
Questions:

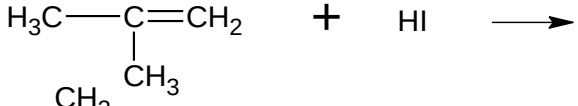
1) Arrange the alkanes in each set in order of increasing boiling point:
   (a) Butane, decane and hexane
   (b) 2-methylheptane, octane and 2,2,4-trimethylpentane

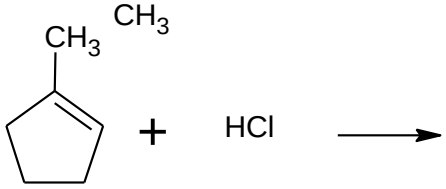
Answers:
1) (a) Butane, hexane, decane. All are unbranched alkanes. As the number of carbon atoms increases, the forces between molecule increases and boiling point increase.

(b) 2,2,4-trimethylpentane, 2-methylheptane, octane. All are constitutional isomers. The relative boiling point depends on the degree of branching. Highly branched chains have lowest boiling point. Unbranched isomers have highest boiling point.

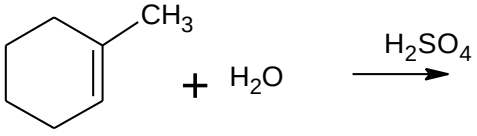
5.3.3 Alkenes
Questions:

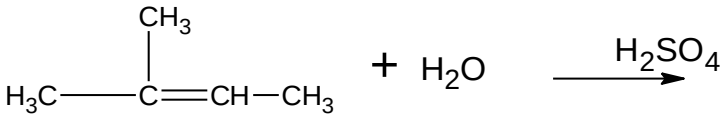
1) Name and draw the structural formula for the product of each alkene addition reaction:

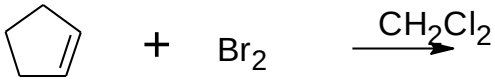
(a) 

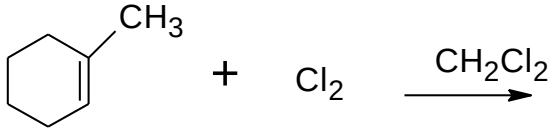
(b) 

2) Draw the structure of the product of each reaction:

(a) 

(b) 

(c) 

(d) 

3) Give the major product formed in each of the following reactions and identify the type of reaction:

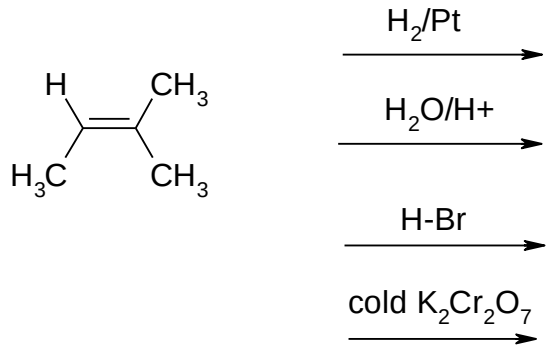
(a) $CH_3Br + CH_3ONa \longrightarrow$

(b) $(CH_3)_3CBr + KOH \xrightarrow[\text{ethanol}]{}$

(c) $(CH_3)_3CBr + H_2O \longrightarrow$

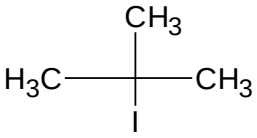
(d) $CH_3CH_2Cl + NH_3 \longrightarrow$

4) Write the major organic products for the following reactions:

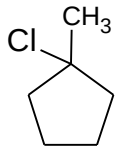


Answers:

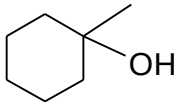
1) (a) 2-iodo-2-methylpropane



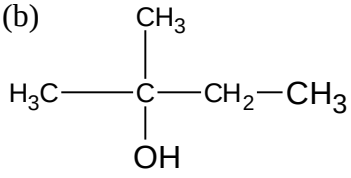
(b) 1-chloro-1-methylcyclopentane



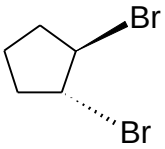
2) (a)



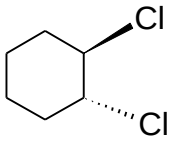
(b)



(c)



(d)



3) (a) $CH_3CHBrCHBrCH_3$, addition

(b) $CH_3CH_2CH_2CH_2CH_3$, addition (reduction)

(c) $CH_2(OH)CH_2(OH)$, addition (oxidation)

(d) $CH_3CH_2CH(OH)CH_3$, addition

(e) $CH_3CH_2CH(Cl)CH_3$, addition

4) (a) $CH_3CH_2CH(CH_3)_2$

(b) $CH_3CH_2C(OH)(CH_3)_2$

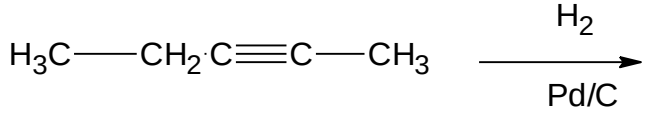
(c) $CH_3CH_2CBr(CH_3)_2$

(d) $CH_3CH(OH)C(OH)(CH_3)_2$

5.3.4 Alkynes

Question:

1) Give the major product in each reaction:

(a) 

(b) $CH_3\text{-}C{\equiv}CH + Br_2 \rightarrow$

(c) $CH_3\text{-}C{\equiv}CH + 2Br_2 \rightarrow$

Answers:

1) (a) $CH_3\text{-}CH_2CH_2\text{-}CH_2\text{-}CH_3$

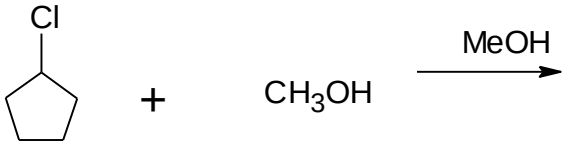
(b) $CH_3\text{-}CBr{=}CBrH$

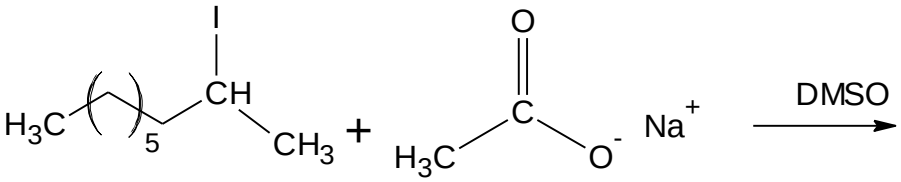
(c) $CH_3\text{-}C(Br)_2\text{-}C(Br)_2H$

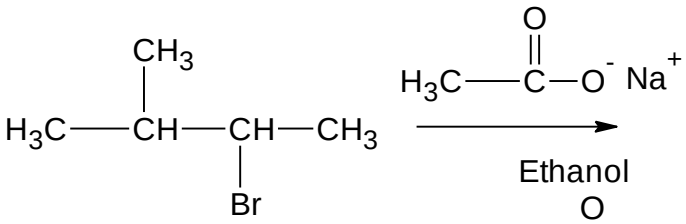
5.3.6 Alkylhalides

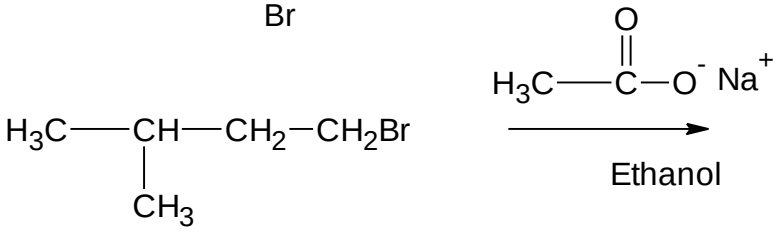
Questions:

1) Give the major product and identify the type of reaction.

(a) 

(b) 

(c) 

(d) 

2) Give the major product formed in each of the following reactions and identify the type of reaction:

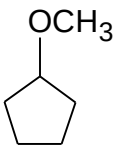
(a) $CH_3Br + CH_3ONa \longrightarrow$

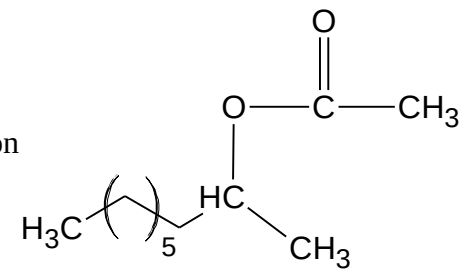
(b) $(CH_3)_3CBr + KOH \xrightarrow[\text{ethanol}]{}$

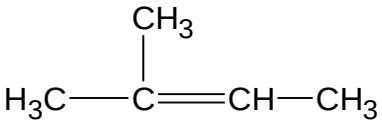
(c) $(CH_3)_3CBr + H_2O \longrightarrow$

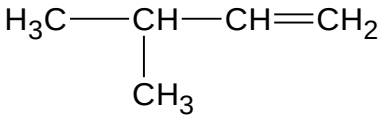
(d) $CH_3CH_2Cl + NH_3 \longrightarrow$

Answers:

1) (a) Substitution 

(b) Substitution 

(c) Elimination 

(d)) Elimination 

2) (a) CH_3OCH_3, substitution

(b) $(CH_3)_2C=CH_2$, elimination

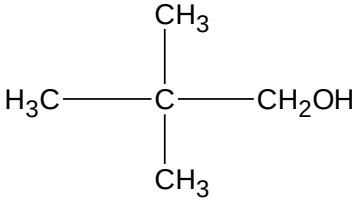
(c) $(CH_3)_3COH$, substitution

(d) $CH_3CH_2NH_2$, substitution

5.3.7 Alcohols

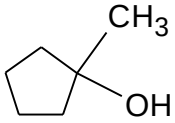
Questions:

1) Classify each alcohol:

(a) 

(b) 

(c) $CH_2=CHCH_2OH$

(d) 

2) Give the products of the following reactions

(a) Dehydration reaction:

(i) CH_3-CH_2-C(OH)$(CH_3)_2$

(ii) $CH_3CH_2CH_2CH_2OH$

(b) Oxidation Reaction:

(i) $CH_3CH_2CH(OH)CH_3$

(ii) $CH_3CH_2CH_2CH_2OH$

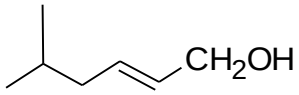
(iii) $CH_3CH_2C(OH)(CH_3)_2$

(c) Formation of alkyl halide:

(i) $(CH_3)_2CHOH$ + HBr $\rightarrow$

(ii) $CH_3(CH_2)_5CH(OH)CH_3 + HCl \rightarrow$

3) Which Carbonyl compound gives the following alcohols:
   (a) $CH_3CH_2CH(CH_3)CH_2CH(OH)CH_3$

   (b) 

4) Predict the organic products of acidic ($K_2Cr_2O_7$) oxidation of
   (a) ethanol (b) 1-butanol (c) 2-butanol

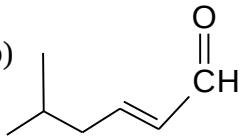
5) Suggest a method for preparing from alcohols
   (a) CH_3CH_2COOH(acid) (b) $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCOCH_3$ (ketone)

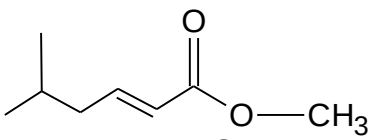
Answers

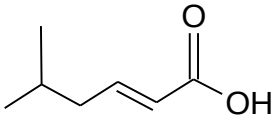
1) (a) Primary
   (b) Secondary
   (c) Primary
   (d) Tertiary

2) (a) (i) $CH_3CH_2C(CH_3)=CH_2$
   (ii) $CH_3CH_2CH=CH_2$
   (b) (i) $CH_3CH_2COCH_3$ a ketone
   (ii) $CH_3CH_2CH_2COH$ a aldehyde and then
   $CH_3CH_2CH_2COOH$ a carboxylic acid
   (iii) no reaction because the alcohol is a tertiary alcohol and tertiary alcohols do not undergo oxidation reaction
   (c) (i) $(CH_3)_2CHBr$
   (ii)) $CH_3(CH_2)_5CH(Cl)CH_3$

3) (a) $CH_3CH_2CH(CH_3)CH_2CHOCH_3$

   (b) 





4) (a) ethanoic acid
   (b) butanoic acid
   (c) 2-butanone

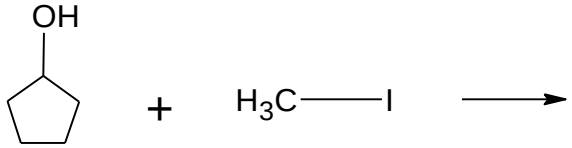
5) (a) $CH_3CH_2CH_2OH \rightarrow CH_3CH_2CHO \rightarrow CH_3CH_2COOH$
$K_2Cr_2O_7$ used as a oxidizing agent

(b) $CH_3CH_2CH(CH_3)CH(OH)CH_3 \rightarrow CH_3CH_2CH(CH_3)COCH_3$
An oxidation of secondary alcohol gives a ketone. Acidified potassium dichromate is commonly used.

5.3.8 Ethers

Questions:

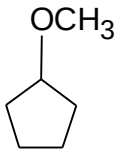
1) Give the products of the following reactions:

(a) 

(b) $(CH_3)_2CHO^- + CH_3CH_2I \rightarrow$

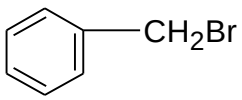
2) How would you prepare the following:
(a) Methylpropyl ether
(b) Benzyl isopropyl ether
(c) CH_3OCH_3
(d) $CH_3CH_2OCH_3$

Answers:

1) (a) 

(b) $(CH_3)_2CHOCH_2CH_3$

2) (a) $CH_3CH_2CH_2OH + CH_3Br$

(b)) $(CH_3)_3COH +$ 

(c) $NH_3 + CH_3COCl \rightarrow CH_3CONH_2$

(d) $NH_3 + C_2H_5COCl \rightarrow C_2H_5CONH_2$

5.3.9 Amines

Questions:

1) Classify the following amines as Primary, Secondary or Tertiary amines

(a) $C_6H_5NH_2$

(b) $(CH_3)_2NH$

(c) $(CH_3)_2CHNH_2$

(d) $(CH_3CH_2)_3N$

(e) CH_3NH_2

2) Give the products of the following reactions:

(a) $CH_3CH_2CH_2COCl + NH_3 \rightarrow$

(b) $CH_3CH_2CH_2COCl + CH_3CH_2NH_2 \rightarrow$

(e) $CH_3CH_2CH_2COCl + (CH_3CH_2)_2NH \rightarrow$

3) Write the structure of amine salts obtained when ethyl amine is treated with HCl.

4) How would you prepare the following amides:

(a) CH_3CONH_2 (b) $C_2H_5CONH_2$

Answers:

1) (a) Primary
(b) Secondary
(c) Primary
(d) Tertiary
(e) Primary

2) (a) $CH_3CH_2CH_2CONH_2$

(b) $CH_3CH_2CH_2CONH(CH_3CH_2)$

(c) $CH_3CH_2CH_2CON(CH_3CH_2)_2$

3) $CH_3CH_2NH_2 + HCl \rightarrow CH_3CH_2NH_3^+ Cl^-$

4) (a) $CH_3COCl + NH_3 \rightarrow CH_3CONH_2$

(b) $C_2H_5COCl + NH_3 \rightarrow C_2H_5CONH_2$

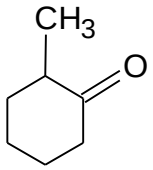
5.3.10 Aldehydes and ketones

Questions

1) How would you prepare the following products via **oxidation:**

(a)$CH_3CH_2CH_2CH_2COH$

(b) $CH_3CH(CH_3)COCH_3$

(c) 

2) Write equations to show the following can be synthesized starting from alcohols:

(a) acetone (b) propanal (c)2-butanone

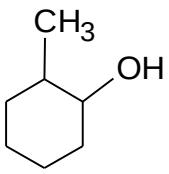
3) How would you differentiate chemically between the following: methanal and propanote?

4) Explain the difference in boiling points of the following: $(CH_3)_3CH$ b.p. -12 ^oC, CH_3COCH_3 b.p. 56 ^oC, $CH_3CH(OH)CH_3$ b.p. 83 ^oC

Answers:

1) (a) $CH_3CH_2CH_2CH_2C(OH)H_2$

(b) $CH_3CH(CH_3)CH(OH)CH_3$

(c) 

2) (a) $CH_3CH(OH)CH_3 \rightarrow CH_3COCH_3$
$K_2Cr_2O_7$ used as a oxidizing agent

(b) $CH_3CH_2CH_2OH \rightarrow CH_3CH_2CHO$
$K_2Cr_2O_7$ used as a oxidizing agent

(c) $CH_3CH(OH)CH_2CH_3 \rightarrow CH_3COCH_2CH_3$
$K_2Cr_2O_7$ used as a oxidizing agent

3) If reacted with acidified potassium dichromate methanal will undergo further oxidation reaction to give methanoic acid. Color change will be noted (i.e colour change from orange to green). There will be no change with propanone if reacted with acidified potassium dichromate. Also aldehyde will react with Tollen's reagent to give a silver mirror and Fehlings solution too give a red precipitate but ketones will not.

4) $(CH_3)_3CH$ is a non polar molecule therefore no dipole diploe interaction. Low boiling point due to weak intermolecular interactions. CH_3COCH_3 has a polar carbonyl group so has dipole dipole interaction. High boiling point due to stronger intermolecular interaction. $CH_3CH(OH)CH_3$ forms hydrogen bond with its own molecule which gives quite high boiling point.

5.3.11 Esters

Questions:

1) How would you prepare the following esters:
   (a) Butyl acetate
   (b) Methyl butanoate

2) Give the products of the following reactions:
   (a) $CH_3CH_2CH_2COOC_2H_5 + NH_3 \rightarrow$

   (b) $CH_3CH_2CH_2COOC_2H_5 + H_2O/H^+ \rightarrow$

3) Write equations to show how the following esters can be prepared:

   (a) methyl-n-butanoate (flavour of apples)

   (b) $CH_3CH_2CO_2CH_2CH(CH_3)_2$ (rum flavour)

4) Show by equations how the following esters react with

   (i) H_2O/H^+ (ii) CH_3CH_2OH/H^+ (iii) NH_3:

   (a) $CH_3CO_2CH_2CH_3$

   (b) $CH_3CO_2CH_2CH_2CH_3$

5) How would you prepare glycerol from a vegetable oil/fat?

Answers:

1) (a) Acetic acid and 1-butanol
   (b) Butanoic acid and methanol

2) (a) $CH_3CH_2CH_2CO\ NH_2 + C_2H_5OH$

(b) $CH_3CH_2CH_2COOH + C_2H_5OH$

3) (a) $CH_3OH + CH_3CH_2CH_2COOH \rightarrow CH_3CH_2CH_2COOCH_3$

(b) $CH_2(OH)CH(CH_3)_2 + CH_3CH_2COOH \rightarrow CH_3CH_2COCH_2CH(CH_3)_2$

4) (a) (i) $CH_3CO_2CH_2CH_3 \xrightarrow{H_2O/H^+} CH_3COOH + CH_3CH_2OH$

(ii) $CH_3CO_2CH_2CH_3 \xrightarrow{CH_3CH_2OH/H^+} CH_3CO_2CH_2CH_3 + CH_3CH_2OH$

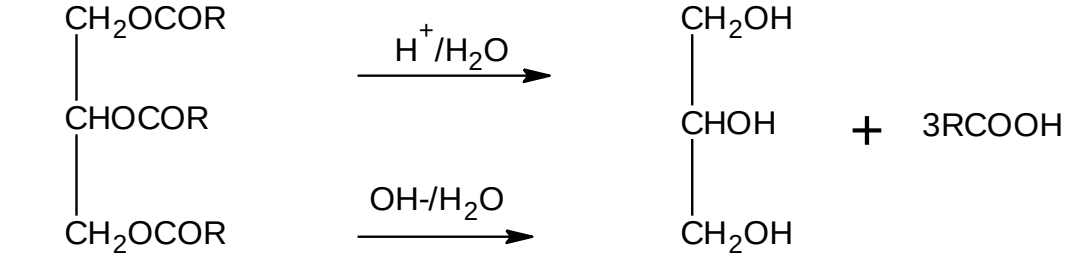
(iii) $CH_3CO_2CH_2CH_3 \xrightarrow{NH_3} CH_3CONH_2 + CH_3CH_2OH$

(b) (i) $CH_3CO_2CH_2CH_2CH_3 \xrightarrow{H_2O/H^+} CH_3CO_2H + CH_3CH_2CH_2OH$

(ii) $CH_3CO_2CH_2CH_2CH_3 \xrightarrow{CH_3CH_2OH/H^+} CH_3CO_2CH_2CH_3 + CH_3CH_2CH_2OH$

(iii) $CH_3CO_2CH_2CH_2CH_3 \xrightarrow{H_2O/H^+} CH_3CONH_2 + CH_3CH_2CH_2OH$

5)



$R = CH_3(CH_2)_{16}$

glyceryl acetate

glycerol